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EVALUATION OF POLLUTION CONTROL IN FOSSIL FUEL CONVERSION PROCESSES. ANALYTICAL TEST PLAN

C. D. Kalfadelis, et al

Exxon Research and Engineering Company

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Conversion	Lurgi Process	14B
Testing	COED Process	
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October 1975

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SUMMARY

A coal gasification process (Lurgi) and a coal liquefaction process (COED) have been used as the basis for preliminary definition of those streams which require analysis to permit an assessment of the pollution potential of the processes in the light of current environmental standards. Methods for sampling indicated streams and analytical procedures which are required to obtain the data have been defined. These summaries may be readily modified or adapted to other processes, and expanded to include additional polluting constituents or improvements in analytical procedures.

TABLE OF CONVERSION UNITS

To Convert From	To	Multiply By
Btu	Calories, kg	0.25198
Btu/pound	Calories, kilogram	0.5552
Cubic feet/day	Cubic meters/day	0.028317
Feet	Meters	0.30480
Gallons/minute	Cubic meters/minute	0.0037854
Inches	Centimeters	2.5400
Pounds	Kilograms	0.45359
Pounds/Btu	Kilograms/calorie, kg	1.8001
Pounds/hour	Kilograms/hour	0.45359
Pounds/square inch	Kilograms/square centimeter	0.070307
Tons	Metric tons	0.90719
Tons/day	Metric tons/day	0.90719

INTRODUCTION

The Environmental Protection Agency has anticipated the pollution potential of fossil-fuel conversion processes and has attempted to define the extent of controls which may have to be applied in the conversion of naturally occurring "dirty" fuels. Thus, a particular goal is to insure that contemplated fuel conversion plants do not themselves become sources of environmental pollution.

Accordingly, the Environmental Protection Agency has awarded Contract No. EPA-68-02-0629 to Exxon Research and Engineering Company to evaluate the current status of fossil fuel conversion and/or treatment processes with respect to pollution control and thermal efficiency. Specifically, Exxon Research and Engineering Company is performing a detailed pollution control assessment of representative processes using nonproprietary information. As a result of this study the "technology needs" to minimize pollution will be delineated in order to allow sufficient time for research, development, and design of adequate pollution control equipment for coal conversion processes.

Few developers of conversion processes have so far seriously addressed pollution control requirements for their process, reflecting the fact that no significant commercial system has yet been constructed in the United States. In general, the thrust of the work which has been reported has been directed to basic process development, including hardware development and yield improvement. And, until recently, much of the developmental effort had been conducted on so small a scale as to make suspect extrapolations of analytical results to commercial systems.

A particular difficulty with fossil fuel systems, and for coal in particular, is the complexity of the composition of streams within the system. Coal has a very complex, vaguely defined organic structure superposed on an equally complex mineral or inorganic base. Thermal processing of such materials gives rise to myriad reaction products whose form and stability are a function of the temperature of processing and of the atmosphere in which the processing is conducted.

The coal itself and many of the primary products of coal conversion plants are unstable in a normal atmosphere. Coal begins to lose occluded gases, and its surface begins to oxidize as it is broken out of the earth. The coal feeds to conversion processes and chars obtained from conversion systems are pyrophoric to some degree. Coal liquids require considerable processing to produce stable end products.

The primary pollutant which most conversion processes intend to control is sulfur. However, most other elements exist in coal, and the opportunity to produce almost every pollutant or pollutant form for which controls have been established is present in most integrated coal conversion systems. It is clear that the list of controlled pollutants will grow, and the probability that new legislation will impact on coal systems is high.

There is, of course, no body of Federal environmental legislation which is specifically directed to coal conversion systems. However, many of the component operations envisioned for such systems are subject to existing regulations, and it is probable that further specific regulations will be enacted as systems come into existence. In fact, it is possible that the "coal conversion industry" may represent the first instance of an industry which is essentially regulated before any substantial industry exists.

The purpose of this study is to establish a baseline for the system of analysis which may be required to assess the pollution potential of a coal conversion facility. It is, of course, geared to present environmental standards and employs established or state-of-the-art sampling and analytical methods. It is obvious that analysis of all relevant streams around an integrated system will constitute a major undertaking in terms of labor and time and will require significant investment in analytical facilities and materials.

1. GENERAL PHILOSOPHY AND APPROACH

1.1 Goals of an Analytical Test Plan

It should be realized at the outset that a coal gasification or liquefaction plant is very complex. Such a plant consists of many units in the main processing stream with numerous auxiliary units necessary for clean, efficient operation. The nature of the central unit for coal conversion differs from process to process. The emerging primary stream is different in each case and this leads to major differences in subsequent processing units.

An example of these differences is very apparent in a comparison of the Lurgi and Koppers-Totzek gasification processes. The Lurgi process (4) operates at intermediate pressures, relatively low temperatures and uses a fairly large sized coal feed. The Koppers-Totzek process (17), on the other hand, operates at low pressure and high temperature and uses a fine sized coal feed. The higher pressure and low temperature of the Lurgi process produces tars, oils and organic compounds containing sulfur and oxygen. The presence of these materials in the Lurgi raw product gas introduces complexities into the clean-up systems that are absent from the Koppers-Totzek process. The presence of low molecular weight paraffins can have an effect on subsequent acid gas removal; the presence of organic oxygen and sulfur compounds introduces restrictions and requirements on dirty process water treatment that have an effect downstream on ultimate water disposal. The large quantity of small particulate matter in the latter process requires special considerations for removal that are absent in the Lurgi process. The need for larger sized feed coal in the Lurgi process causes a special problem of fines disposal from the grinding operation.

The many alternatives existing for subsequent gas treatment and auxiliary units leads to further overall complexity. For example, numerous processes exist for acid gas removal (necessary in all gasification and liquefaction schemes). (For more details see, for example, reference 2. There are processes utilizing absorption and reaction of the acid gases with a suitable basic solution (e.g., hot carbonate; amines) followed by regeneration. Other processes use low temperature absorption with a suitable solvent (e.g., methanol, propylene carbonate, etc.) followed by desorption. A third technique involves absorption of hydrogen sulfide into an oxidizing solution where the hydrogen sulfide is converted to sulfur. Still a further variation involves removal of the sulfur in situ with an appropriate solid basic material such as limestone or dolomite (25). All of these alternatives lead to further options or requirements on subsequent treatment of the acid gases to remove sulfur.

In the case of auxiliary units many different alternatives exist depending on the initial gasification or liquefaction technique. An example is the fuel to be used in steam production. Coal can be used as fuel with appropriate stack gas scrubbing. Some processes produce chars that are available for fuel; some processes produce liquid products that can be burned.

Another alternative is the use of clean product gas or liquid; sulfur removal from stack gases is thus avoided. Another example of an auxiliary unit with many alternatives is the treatment of waste water. Alternatives such as biox ponds, adsorption with solids, etc. again add complexity to the subject of environmental control.

The myriad of alternatives available for coal conversion plants makes it essentially impossible and certainly non-productive to attempt to anticipate all permutations and combinations of process units in an analytical test plan. Such a test package would be so large that it would confuse rather than aid in the gathering of meaningful analytical data.

The approach taken in devising the analytical test plan presented here was to choose "representative" processes that exemplify the three basic requirements for obtaining a satisfactory description of the flow of materials. These requirements are choice of process streams, choice of stream components to be determined and method of analysis.

Two major levels of information are available from the choice of streams: those streams may be chosen that give an overall material balance for the plant or the streams can be chosen to give, besides an overall balance, a balance around each major unit of the plant. For environmental purposes it is only necessary to know what goes into the plant and what comes out of the plant. This should offer the lowest cost assessment of the plants effect on the environment. Realistically however, a number of factors make such a simple determination very difficult. An example of the difficulties is a determination of cooling tower effluents (in vaporization and drift). Since the wind velocity and direction affect the spot concentration of effluents, sampling and data treatment are very inaccurate. Because cooling tower effluent is very large, errors in the determination of the composition of the effluent can seriously affect the overall plant material balance.

In this analytical test plan, the problem of overall vs. unit material balances has been addressed in a way that will minimize costs for a given objective. First, those streams have been identified that would give an overall plant material balance. Should the balance be closed on appropriate analysis of these streams then that is sufficient. In all probability this will not be the case. Therefore, those units around which a material balance should then be made have been listed individually with an indication of streams to be analyzed. This will allow a determination of the source of errors in the overall balance and appropriate corrections can be made. It should be pointed out that the judiciousness of the choice of units where errors will appear can have a major effect on the costs associated with this endeavor. Experience is invaluable in making a decision as to what units should be examined in detail.

As indicated earlier, it is next to impossible to document all streams for every combination of plant units. It is believed, however, that the examples included in this test plan are sufficiently general that an experienced person can make the necessary revisions to fit the plant under evaluation. This analytical test plan is therefore designed for use by such skilled personnel. Only minor modifications, together with a few added or deleted streams, will be necessary for a specific plant.

The choice of stream components for which analyses are necessary is very subjective. Again, costs may be the limiting factor in making this choice. The list of components in this test plan for which analyses are to be made represents what is felt to be a reasonable choice that should be determined and that can be determined without an inordinate expenditure of funds. However, there is almost no limit to additions that can be made to the list. (A few deletions may also be made in some cases.)

The choice of sampling and analytical techniques to be used in determining the concentration of selected components in the streams is somewhat arbitrary. The techniques outlined in this test plan were selected on the basis of the five considerations detailed in Section 7.1 and the experience and knowledge of the factors involved in such determinations. In all such work however, the techniques may have to be changed to fit a specific situation. These changes may be necessary due to interference from other components in the stream, unusual concentration ranges, or others and can only be recommended for very specific cases by experienced personnel.

The goal of this analytical test plan is to supply sufficient information for example process and analytical techniques to allow experienced personnel to rapidly and easily modify the plan to fit the process of interest. Streams comparable to those in the present test plan can be identified, and additions and deletions can be made where appropriate. The decision should be made as to what components are necessary for the desired material balance and what other components are of interest, and appropriate sampling and analyses can then be performed. A trial plant material balance should be made. If this balance cannot be made, then individual units will have to be investigated to determine the source of errors. Once the source and magnitude of errors have been identified, a complete balance should be possible. Future balances are then much simplier since errors are known before hand.

In some cases, for environmental control purposes or for other reasons, it may be necessary to extend the analyses to include all input and output streams from one particular unit. This could be the case, for example, when comparisons need to be made between two types of control technology. Then, all streams around that unit would be sampled and analyzed according to the test plan. No attempt is made in this plan to point out such units as they will vary from case to case.

It is anticipated that an analytical test plan, modeled along the lines outlined in this report, will furnish accountability for all pollutants of interest that may enter the plant in the coal, water, chemicals, etc., or that may be formed during processing.

1.2 Specific Approach

Two processes, one for coal gasification and one for coal liquefaction, have been chosen as representative of their respective classes for the purpose of establishing a baseline analytical system. These processes are the Lurgi process as representative of gasification and the COED process of FMC for liquefaction.

In the case of gasification, the Lurgi process was chosen because environmental impact statements have been prepared by domestic concerns who propose to construct integrated commercial facilities (1,2,3), because the process was reviewed in an earlier phase of this program (4), because a number of commercial facilities are in operation in other countries (5), and because almost all units of gasification processes are present. This information provided an opportunity to assess the environmental impact and the effectiveness of controls in widely differing situations.

There is unfortunately no such clear-cut candidate for a coal liquefaction system. The COED (pyrolysis) process was chosen because of the large body of information which is available in the public literature (6-15), because this process was also reviewed in an earlier phase of this program (16), and because an integrated COED facility would probably include most component operations required by other proposed coal liquefaction schemes.

Each component operation of each process is described, including the approximate composition of incoming and outgoing streams, where these are known. The process descriptions are not intended to be taken as definitive, and much more detailed information is available in the references cited. Streams which may be analyzed, especially those streams which may impact on the environment, are indicated. Sampling procedures, sample treatment, and analytical methods are described using established or state-of-the-art technology.

The Lurgi process streams impacting on the environment are outlined in detail, with quantities of material where available. Information is included on actual analysis of some of these streams together with analyses of comparable streams from other processes where available. Included for information and comparison are existing or proposed state and Federal regulations concerning quantities of pollutants allowed. A discussion of problem areas is given with an indication of other streams for which analytical data may be necessary for an accurate assessment of environmental impact. A sample data sheet is included that will serve as a guide in data acquisition.

The COED process streams are similarly treated as an example of liquefaction. The amount of information available is much less for the COED process than for the Lurgi process since no commercial plant is yet in operation. Information in the Lurgi section can, by analogy, be applied to the COED process.

1.3 Operating Conditions and Flow Rates

Information on typical operating conditions and flow rates are given for each unit of interest. If more detailed information is required, references have been given to process reports giving this information in detail. Differences in operating conditions and flow rates will not affect the testing procedures in most cases. If quantities of potential pollutants are less than can be determined by the procedures outlined in this test plan, then they may be insignificant. If it is eventually decided that extremely low concentrations must be determined then that particular concentration range must become a research program itself.

1.4 Determination of Effect on Environmental Factors of Altered Operating Conditions

In some cases it may be of interest to determine what effect, if any, altered operating conditions may have on environmental factors. For example, hydrogen cyanide and ammonia formation will be affected by reactor temperature and pressure. In most cases, limits exist as to the change in operating conditions that can be effected. These limits are set by such factors as reaction rate, materials of construction, etc., and, for a given design, are narrow.

To obtain a good picture of the effect of operating variables on pollutant production, it is necessary that the conditions be changed sufficiently so that the change in pollutant concentration is significantly measurable and that three levels of concentration be measured. It is thus suggested that operating conditions be changed by at least $\pm$ 10% and that the pollutant concentrations be determined at these levels. Thus, if the reactor normally operates at 1000°F, then data should also be collected at 900°F and 1100°F. In pilot unit operation, such changes will normally be a part of the program in process development. In commercial plant operation, efficiency could well be affected by changes from the design optimum.

It frequently will be necessary to change two or more variables simultaneously when a change is desired. Thus, lowering the temperature must usually be accompanied by a decrease in feed rate since reactions are slower. Each such change must be examined individually and in detail to assure process operation.

Variables that may be changed to determine the effect on pollutants may be summarized. In the reactor, the temperature, pressure, oxygen-steam-coal ratios and feed rate may be altered. A change in the ratio of raw gas to quench liquid may cause a change in pollutant output. In the shift section, changes in operating temperature, pressure, and residence time may be significant. Also, when part of the gas by-passes the shift reactors, it would be of interest to determine the effect of changing the ratio of by-pass gas to reacted gas. (The total CO/H_2 ratio must, of course, remain approximately the same.)

In the gas purification section, altering the temperature, pressure and gas to absorbent ratio could be informative. It is doubtful if useful environmental data could be obtained by varying conditions in the methanation section.

It will be of definite interest to change the coal feed to the process. At present, the prediction of sulfur forms in the raw gas seems not to be feasible and the same may hold true for trace elements. Therefore, predictions of the fate of these materials can only be determined empirically. With sufficient data, a correlation might be possible.

2. COAL GASIFICATION

2.1 System Basis

The Lurgi process has been chosen as representative of the class of systems which may be used to produce primarily clean gaseous fuels from coal. There is of course a very wide range of processing conditions which may be applied to coal to generate gas. These range from virtually standard atmosphere and temperature, as in diminution of total pressure on some coals to recover occluded methane, to virtually complete gasification of all organic matter at high temperature, as in the 3300 F steam-oxygen atmosphere of a Koppers-Totzek gasifier (17). The number of proposed processing schemes is large (18,19,20), and the range of products which may issue from the various systems, in addition to noncondensable gases, is extremely broad. It is in fact this broad product spectrum, common to all processing schemes excepting those which operate at very high temperatures, which gives rise to much of the indicated control which must be included in the processing sequence. If an objective is to conserve or produce the high energy-density constituents which may be derived from coal, such as coal liquids or methane equivalent, then processing conditions must be less vigorous than those which decompose or destroy these materials; and, in general, the processing sequence is rendered more complex, the pollution potential is higher, and the conversion efficiency is reduced.

There are a number of variants of the Lurgi process depending on feed and on end-use requirements, and the processing elements, including the gasifiers (21), are undergoing almost constant development. We have chosen the processing scheme proposed for the El Paso Burnham complex (1,2,22) as the particular example of an integrated Lurgi system which may be designed to meet domestic energy/environmental standards. The system proposed by Wesco (23) is practically identical, utilizing essentially the same feed coal and producing the same end products. For purposes of illustration only, we have indicated throughout Section 3 the magnitude of the streams as indicated in El Paso's proposal.

2.2 Process Basis

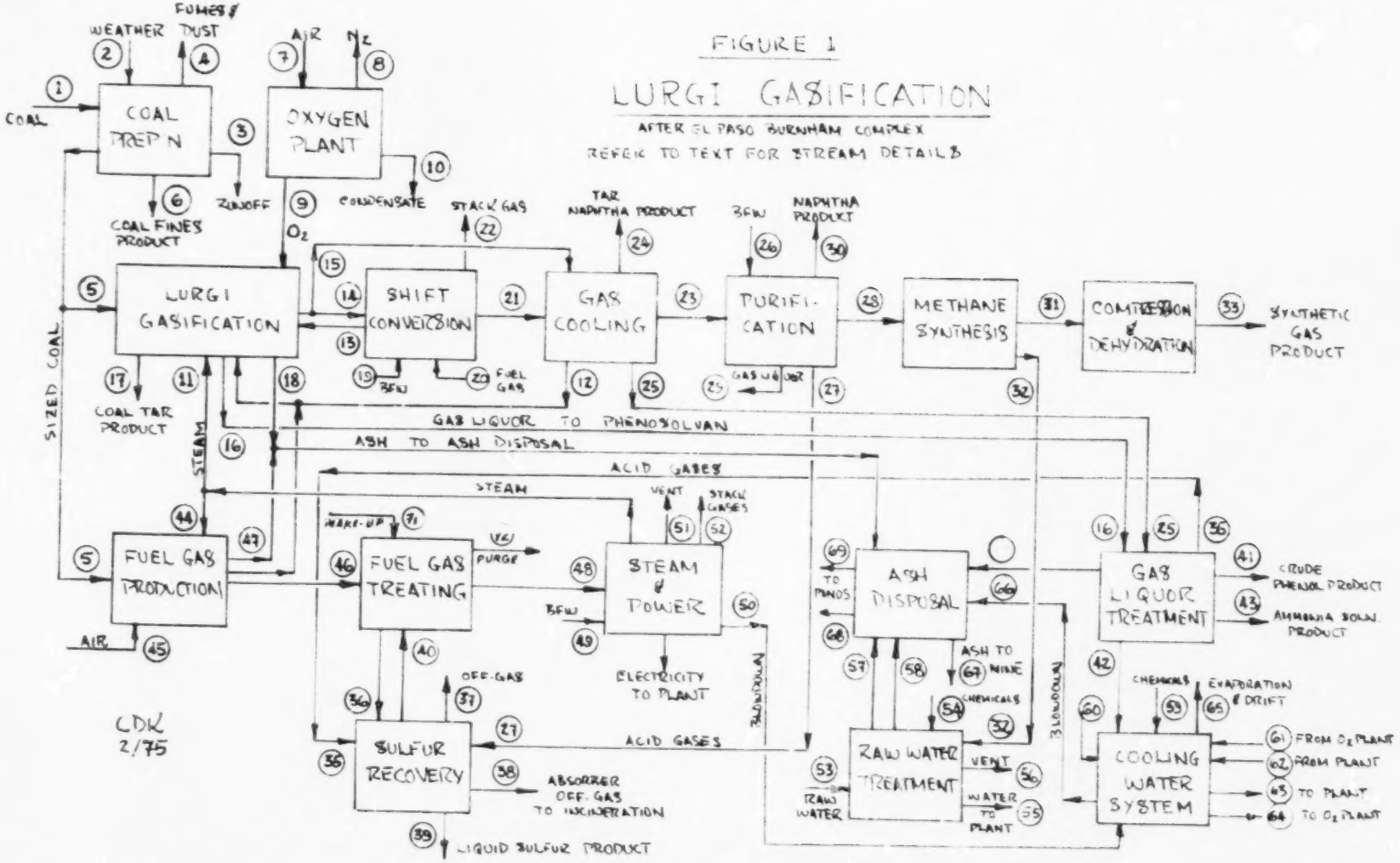
Figure 1 is a schematic representation of the overall processing scheme. The Burnham complex is designed to produce 288 MM scfd of synthetic pipeline gas (954 Btu/scf) from Navajo coal using Lurgi coal gasification, purification, and enrichment technology. Specifically, Lurgi supplied the process design basis for the operations of coal gasification, shift conversion, gas cooling, gas purification, gas liquor treatment, and methanation. In addition, commercial air-separation processing will be included to produce 98 percent purity oxygen for the Lurgi gasifiers, and the Stretford process (British Gas Council) will be used to remove H_2S from acid gases separated from product gas in the gas purification section.

FIGURE 1

LURGI GASIFICATION

AFTER EL PASO BURNHAM COMPLEX

REFER TO TEXT FOR STREAM DETAILS



CDK
2/75

Analysis of the feed coal for the complex is shown in table 1 including two estimates of trace element composition.

In addition to product SNG, the complex will produce the following byproducts:

Product	Quantity
Coal Tar	239,250 GPD
Tar Oil	157,370 GPD
Naphtha	74,900 GPD
Crude Phenol	32,470 GPD
Sulfur	167 TPD
Ammonia Solution	332,550 GPD

The system is designed to be self-sufficient with respect to utilities:

Water

Raw water will be supplied from the San Juan River at a location approximately 40 miles from the plant site. Pipeline and pumping facilities will be provided to transfer the water to the complex where it will be stored and used as required.

Electricity

On-site power generation will be used to supply all power requirements for the complex. Power for the mining operations and the river water pumping systems will be purchased. Power required for crushing and screening of the coal will be exported to the mine.

Steam

Steam will be used in the complex both as a motive force and as a reactant in the gasification processes. All steam generation will be done onsite with a combination of heat recovery and gas-fired boilers.

Fuel Gas Production

Low Btu-content fuel gas will be produced in the complex for use in gas turbines, process heaters, steam superheaters, and power boilers. Airblown Lurgi gasifiers will be utilized in the fuel gas production.

Table 1

NAVAJO SUB-BITUMINOUS COAL (1)

Feed to Burnham Complex

Proximate Analysis	Weight %
DAF coal	66.2
Ash	17.3
Moisture	16.5
Component Analysis (DAF Coal)	
C	76.72
H	5.71
N	1.37
S	0.95
O	15.21
Trace compounds	0.04

HHV range 7500 To 10,250 Btu/lb

	Trace Elements ppm by weight (1)		IGS data*
	Minimum	Maximum	
Sb	0.30	1.20	0.3
As	0.10	3.00	1.3
Bi	0.00	0.20	---
B	60.00	150.00	17.
Br	0.40	18.00	0.4
Cd	0.20	0.40	< 0.2
F	200.00	780.00	39.
Ga	0.50	8.00	1.6
Ge	0.06	0.50	2.
Pb	1.40	4.00	4.
Hg	0.20	0.35	0.06
Ni	3.00	30.00	5.
Se	0.08	0.21	1.2
Zn	1.10	27.00	15.
Be	---	---	0.2
Co	---	---	7.
Cr	---	---	5.
Cu	---	---	22.
Mn	---	---	6.
Mo	---	---	2.
P	---	---	125.
Sn	---	---	< 2.
V	---	---	17.
TOTAL	267.3	1023	

* Data furnished by EPA from Illinois State Geological Survey Analyses of Navajo County Red Seam Coal.

Miscellaneous

Other utilities, such as sewage facilities, fire protection facilities, instrument air, etc., will all be provided in the utility systems to ensure self-sufficiency for the complex. The mine office will be provided potable water, fuel gas, electricity, and sewage facilities from the complex.

3. GASIFICATION PROCESS DESCRIPTION

3.1 Qualifications

Although El Paso's design for the Burnham Coal Gasification Complex (1) has been chosen as the basis for the coal gasification analytical system, most gasification processes (20) will require many of the same major and auxiliary operations provided in the integrated Lurgi plant. Relatively minor modification will be required to adapt this environmental test system to many of the most well-known candidates for coal gasification, assuming that a realistic integrated design is available. Hence, an integrated Synthane design (24) differs primarily in the pressure regime and mode of operation of the gasifiers, required coal communition, and in the particular methanation procedure that is proposed. Other processes may be less complex, especially if methanation facilities are not included or if only low-Btu gas is produced, cf Koppers-Totzek Process (17). And some processes may prove more complex, requiring additions to the analytical scheme, cf. CO_2 Acceptor Process (25) which requires additional facilities for preparing and moving limestone or dolomite through the process. The modifications to the analytical scheme which may be required for a particular process or design will be readily apparent in most instances.

Each processing step or operation in the Lurgi/El Paso design is briefly described below. Significant input and output streams around each operation are described, and the particular streams requiring analysis are designated. The suggested analytical procedures for each stream are referenced to the Analytical Section via table 18.

Note that the plant operator will require other additional analyses to facilitate his operations and insure product specifications. Our concern is only with potential pollutants which may impact on the environment.

Each operator of a coal conversion facility may ultimately be required to account for the disposition of elements present in feed coals whose toxicity or ultimate impact on the environment warrants control. Particular sanctions relating to such potentially toxic discharges, including those relating to atmospheric discharges, discharges to waterways, disposition of solid wastes, and limiting concentrations in work areas, are still in process of formulation (26,27,28,29). However, it is almost certain that the list of controlled substances will grow and that permissible levels in effluents will continue to be limited.

We have accordingly indicated that all generated effluent streams, including products, be analyzed for particular trace element composition, along with feed coal, to permit a gross indication of the disposition of such elements. Streams to be analyzed are shown in the following figures and tables with an asterisk (*). We caution that overall balances for particular elements may be extremely difficult and costly to obtain around an operating system of the type and size under consideration. The complexity of the chemical system, the difficulties associated with representative sampling of very large streams, and the imprecision of available sensors or test methods for the monitoring of trace elements all militate against achievement of

perfect balances. Moreover, the capacity of a large physical system to trap out various elements or compounds, as by chemical combination with materials of construction or through physical condensation or deposition introduces another order of complexity, especially if process changes can result in sudden large emissions.

The "time constant" of the contemplated systems may be very large indeed, and the time rate of change associated with processing conditions for a particular unit will have to be taken into consideration by the analyst if his objective is to obtain a consistent overview of the process. The "steady-state" condition implied in this analytical scheme is very difficult to obtain in practice, especially if batch-type or step-function operations, such as the step-wise addition of coal to the gasifiers, are superposed on an otherwise continuously operating flow train. And it may ultimately be necessary to examine the materials of construction and to physically examine the interiors of vessels or piping for deposited matter to close the balances in some cases.

All facilities of the type under consideration will include a flare system to handle emergency discharges from pressurized vessels and piping. To insure compliance with hydrocarbon emission rates in the future, it may be necessary to size the flare system to handle the entire plant output. The analytical scheme assumes zero discharge at the flare.

Similarly, all such systems will include tankage for storage of liquid byproducts. Presumably standards of performance now imposed on storage vessels for gasoline, crude oil, or petroleum distillates (30) to limit hydrocarbon emissions will apply.

Finally, the operator of a physical plant will be aware that there may be hundreds of valves, packing glands, seals, and other closures through which harmful pollutants may be accidentally discharged. There is no practical remedy for such eventualities except vigilance.

3.2 Coal Preparation (Figure 2 and Table 2)

Coal preparation for the gasification plant will consist of stockpiling, secondary screening, reclaiming, and sampling facilities. The mine will have facilities, for receiving coal from trucks, crushing, and primary screening. The facilities at the mine will be interconnected to those at the gasification plant by a continuous belt conveyor.

Coal, sized at the mine to 1-3/4" x 0", will be received by a conveyor belt connecting the mine and the gasification plant and will be distributed by stacker/reclaimer conveyors for blending and storage.

The coal sampling and stockpiling facilities, which operate less than 24 hours per day, are sized for 3600 tons per hour (tph), while the reclaiming and screening facilities are sized for 1500 tph. The gasification plant will require 1180 tph when operating at full load, and the fuel gas production area will require 208 tph additional.

Six storage areas, each 1750 feet long by 124 feet wide and containing 120,000 tons of coal, will provide blending for Btu control of gasifier feed and approximately 12 days live storage at full capacity operation.

The original design (1) included facilities for briquetting coal fines (<3/16") separated in the screening operations. The briquetting plant included facilities for mixing coal fines with gasifier tar binder and compacting the mix into briquettes which could be charged to the gasifiers along with sized coal. This system has been deleted in the revised design (2), and it is implied that coal fines will issue as a saleable additional product. Fines are generated at the rate of 176 tph.

Prior to sale, the fines are (2) indicated to be directed to a cleaning plant which will separate some 70 tph of refuse. Refuse will be sent to the coal mines for reburial along with gasifier ash. Facilities for collection and/or storage of the product fines has not been specified.

The original design also included emergency stockpile and reclaiming facilities for 650,000 tons of additional sized coal; this emergency storage has been deleted in the revised design.

Wet-scrubber dust collectors will be installed in the secondary screening plant to eliminate dust and fume emissions. Sprays will be used at transfer points for dust suppression.

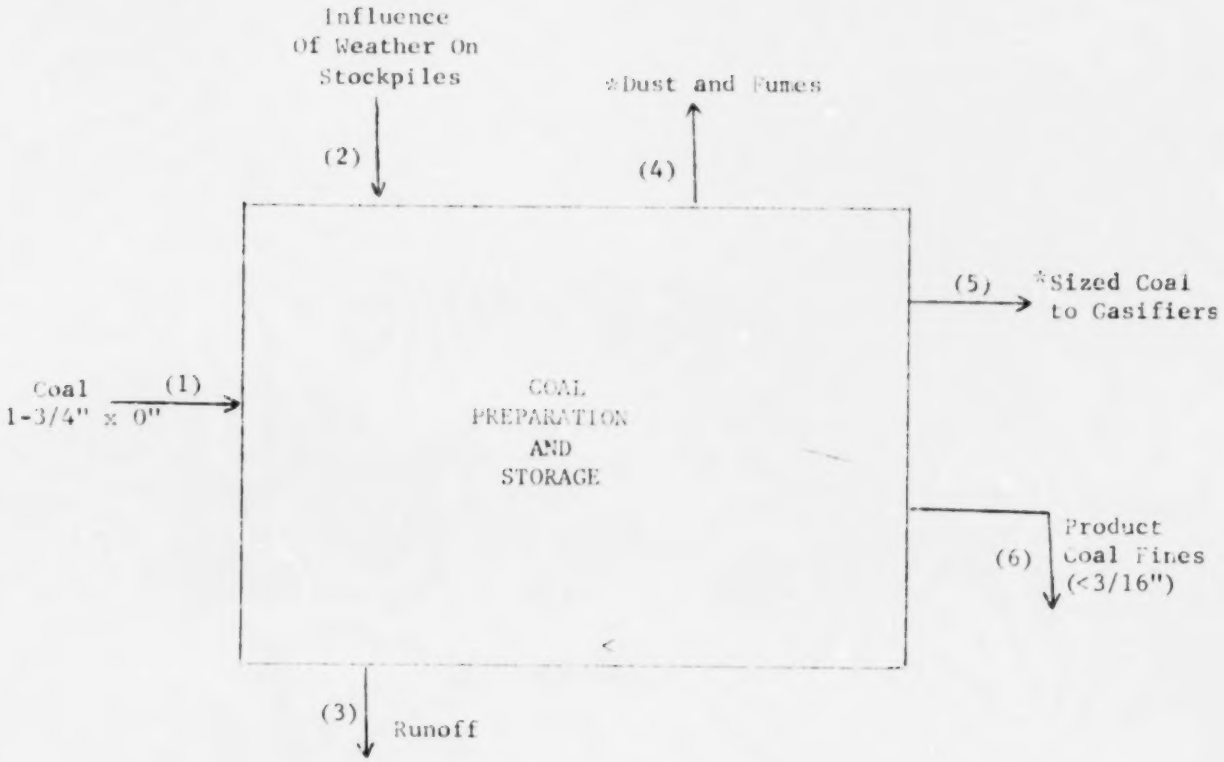


Figure 2

Coal Preparation for Lurgi Plant

Table 2

Coal Preparation for Lurgi Plant

Inlet Streams

(1) Coal, Navajo Sub bituminous; 3600 tph (not used 24 hours per day).

(2) Influence of Weather on Coal Stockpiles and Open Coal Operations.

Outlet Streams

(3) Precipitation Run off to Holding Ponds. May include wet scrubber aqueous effluents.

*(4) Dust and Fumes. Atmosphere in enclosed working areas to be analyzed per Table 18 for particulates. Discrete stack emissions to atmosphere from enclosed spaces and from dust collection equipment to be analyzed per Table 18 for particulates. Atmosphere in vicinity of coal stockpiles, open conveying and handling equipment, and coal fines product collection system to be analyzed per Table 18 for particulates.

*(5) Sized Coal to Gasifiers; 1180 tph and to Fuel Gas Production, 208 tph. To be analyzed as feed coal per Table 18.

**(6) Product Coal Fines, 176 tph. 106 net tph cleaned coal fines to sales. 70 tph refuse directed to mine for burial with gasifier ash.

* Analytical samples, see Table 18.

** Not included in Table 18; however, potential pollution at the mine will have to be addressed.

3.3 Oxygen Production (Figure 3 and Table 3)

The oxygen plant is designed to produce 5650 tons per day of 98% minimum purity vapor phase oxygen.

Atmospheric air will be filtered and compressed to 90 psia in parallel low-Btu gas turbine/steam turbine-driven centrifugal compressors.

Intercooling between the first and second cases and aftercooling after the second case will be utilized and will remove approximately 130 gpm of water which will be recovered for use elsewhere. The relatively dry air (0.5% moisture content) will be delivered to parallel cold boxes.

Air entering the cold box will be cooled to liquefaction temperature by a combination of heat exchange and expansion in a conventional air separation cycle. Once in the liquid state, oxygen and nitrogen will be separated by fractionation. The nitrogen (plus a small quantity of moisture, CO_2, and oxygen) will be regasified in the heat exchange process and its energy utilized before rejection to atmosphere. The liquid oxygen will be gasified to feed the steam turbine-driven oxygen compressors. These centrifugal units will raise the pressure level to 500 psig and deliver 5620 tons per day of oxygen to the Lurgi coal gasifiers. The expansion process in the cold boxes will generate a total of about 500 kW each at full capacity.

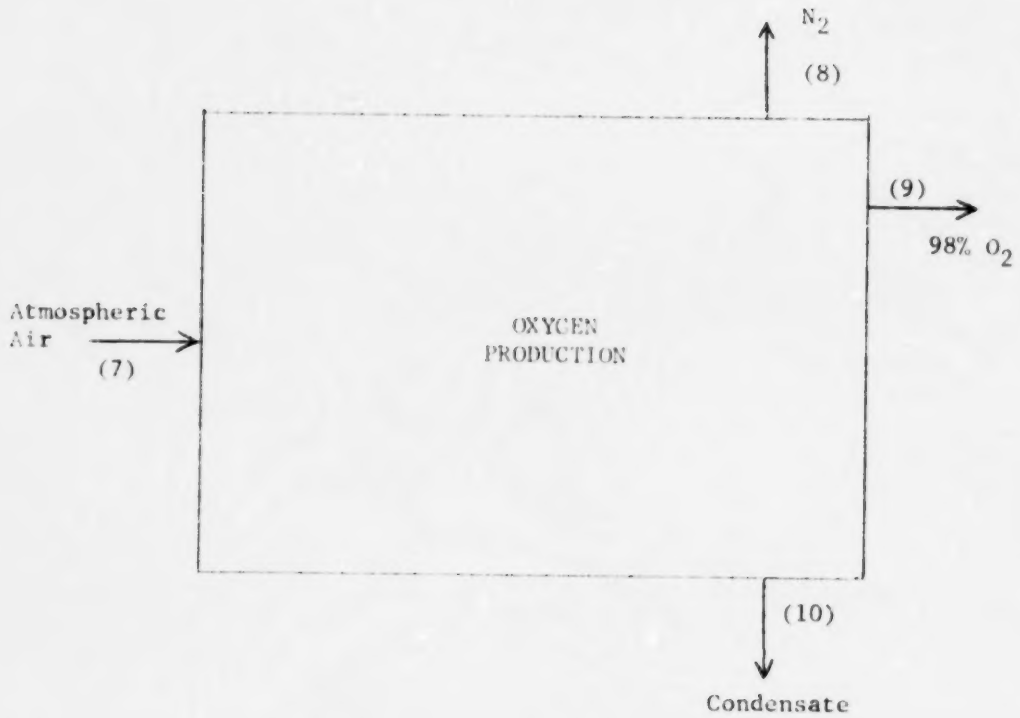


Figure 3

Oxygen Production

Table 3

Oxygen Production

Inlet Streams

(7) Atmospheric air; 500,000 acfm.

Outlet Streams

(8) Nitrogen and other components of air; 794 tph discharged to atmosphere.

(9) 98 percent minimum purity vapor-phase oxygen to gasifiers; 235 tph.

(10) Water condensate from entering air; 125 gpm, to BFW treating.

3.4 Coal Gasification and Gas Liquor Separation (Figure 4 and Table 4)

Navajo coal will be gasified with oxygen and superheated steam at high pressure. This process will produce a raw gas of the following composition:

Component	Volume %
CO_2	28.03
H_2S	0.37
C_2H_4	0.40
CO	20.20
H_2	38.95
CH_4	11.13
C_2H_6	0.61
N_2+AR	0.31
	100.00

Coal will be conveyed from the coal preparation area to coal bunkers located above the coal gasifiers. The coal will be fed to the gasifiers through coal locks, which will be pressurized by a slip stream from the gas cooling area. (Disposition of this gas is discussed later.)

The Lurgi gasifiers are water-jacketed vessels. Oxygen and process steam will be mixed and introduced into the bottom of the gasifiers. The gasifiers will be operated at about 445 psig. Raw gas leaving the gasifiers will be cooled rapidly by quenching with a gas liquor spray in wash coolers. Ash will be removed from the bottom of the gasifier through ash locks and conveyed via water to the ash disposal area.

Raw gas leaving the wash coolers will be cooled to about 370°F in the waste heat boilers which produce 112 psia steam. Some of the liquid condensed in the waste heat boilers will be recycled to the wash coolers, and the excess will be drawn off to the gas liquor separation unit.

In addition to this excess liquor from gasifiers, the gas liquor separation unit will receive gas liquor from the gas cooling area. The gas liquor at high pressure will be flashed to atmospheric pressure in an expansion vessel to remove dissolved gases. The heavy tar will be settled out in a subsequent settling vessel and sent to product storage. The gas liquor, free of heavy tars, will be sent to the gas liquor treatment area to remove dissolved phenol and ammonia.

Raw gas leaving the gasifier section will be divided into two streams; one will be sent to shift conversion and the other will bypass the shift conversion area and will go directly to gas cooling. Crude gas vented from the cyclic operation of the coal locks, the expansion gas, and small quantities of recycle gas from other areas will be compressed and injected into the main stream in the gas cooling area. The recycled vent gas stream from downstream sections and the lock gas stream from the gas cooling area are not shown in Figure 4.

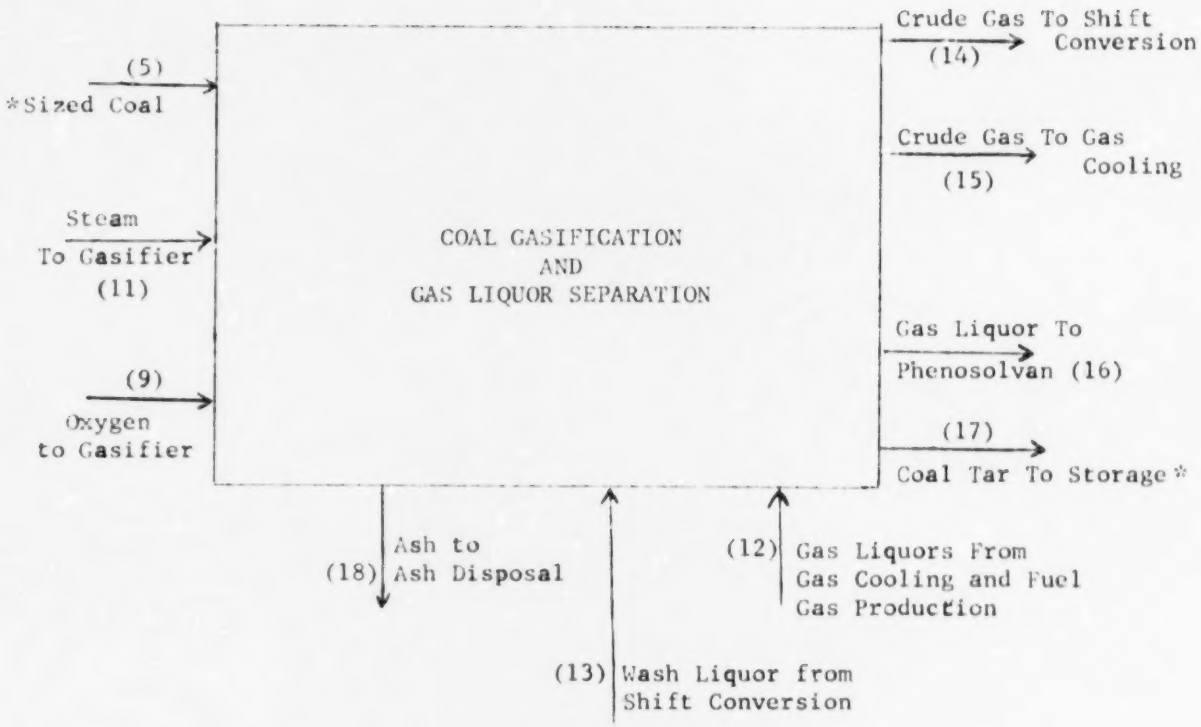


Figure 4

Coal Gasification

Table 4

Coal Gasification

Inlet Streams:

*(5) Sized coal from Coal Preparation; 1180 tph.

(9) Oxygen from Oxygen Plant; 235 tph.

(11) Steam; 1,784,000 pounds per hour.

(12) Gas Liquors from Gas Cooling and Fuel Gas Production recycled to gas liquor separator.

(13) Wash Liquor from Shift Conversion recycled to gas liquor separator.

Outlet Streams:

(14) Crude Gas to Shift Conversion; 623 tph dry basis.

(15) Crude Gas to Gas Cooling; 516 tph dry basis.

(16) Gas Liquor to Phenolsolvan.

*(17) Coal Tar to Tar Product Storage, analyzed for trace elements per Table 18.

(18) Ash to Ash Disposal; 186 tph dry basis.

* Analytical Sample, See Table 18.

3.5 Shift Conversion (Figure 5 and Table 5)

The shift conversion area is designed to produce hydrogen by the "water gas shift" reaction:

$$CO + H_2O = CO_2 + H_2 + 16,538 \text{ Btu per pound mole}$$

Production of this additional hydrogen will be required to adjust the H_2:CO ratio for proper feed to the methanation plant.

Approximately one-half of the total crude gas will be subjected to shift conversion. The balance will be bypassed directly to the gas cooling area. The ratio of the two gas streams will be adjusted to achieve the desired H_2:CO ratio.

Crude gas feed to the shift conversion area will first be cooled in a waste heat boiler. The cooled gas will then be heated in a series of heat exchangers before passing through a prereactor to retain carbon-containing residues. The heated gas will enter the first shift reactor where the bulk of the carbon monoxide will be catalytically converted. Condensed gas liquor will be recycled to the wash cooler in the gasification area.

The first stage hot gas effluent will be cooled in countercurrent exchange with the feed gas before entering the second shift reactor where further conversion of carbon monoxide will take place. The effluent gas from the second shift reactor will be cooled by exchange with feed gas before leaving the shift conversion unit.

A shift startup heater will be located in a bypass between the prereactor and first shift reactor. The heater is indicated to be fired with washed crude gas taken from the main stream ahead of the prereactor.

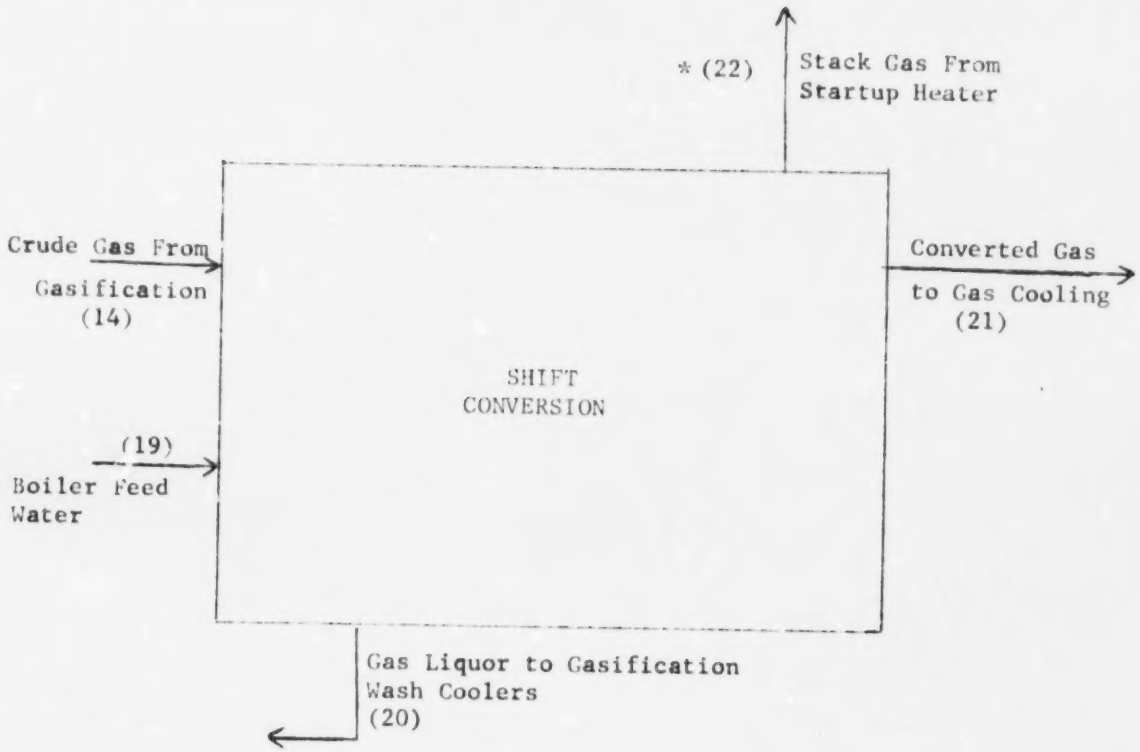


Figure 5

Shift Conversion

Table 5

Shift Conversion

Inlet Streams:

(14) Crude Gas from Gasification; 625 tph dry basis.

(19) Boiler Feed Water.

Outlet Streams:

(20) Gas Liquor recycled to Gasification area.

(21) Converted Gas to Gas Cooling; 696 tph.

*(22) Stack gas from Shift Startup Heater, to be analyzed as combustion stack gas per Table 18. Note: This stream exists only during shift plant startup periods.

* Analytical Sample, see Table 18.

3.6 Gas Cooling (Figure 6 and Table 6)

The gas cooling area will cool the hot gases from gasification and shift conversion before they are fed to the low-temperature purification area. The cooling scheme will be arranged to recover and utilize as much of the process heat as is practical. The gas cooling will be accomplished in parallel trains. Each train will be further subdivided into two lines of exchangers, one for cooling the crude gas bypassing the shift conversion area, and the other for cooling the converted gas, to provide improved heat recovery efficiency.

Crude gas will first be cooled in a waste heat boiler generating steam at about 76 psia. Further cooling will be accomplished in a low-pressure steam generator. The gas will then be cooled in a precooler by an air cooler. The gas will finally be cooled by cooling water.

The hot gas liquor and tar which will be condensed during cooling in the waste heat boiler and the low-pressure steam generator will be recycled to the primary gas liquor separator in the gasification area. The remaining condensate streams, which will be comprised of gas liquor and a tar oil naphtha mixture, will be gathered and separated in a second gas liquor separation unit.

Converted gas from the shift conversion will first be cooled by exchange with high-pressure boiler feedwater; then in series by generating low-pressure steam. The gas will then be cooled by an air cooler. Final cooling will be by cooling water.

Gas liquor and tar condensate from the converted gas in the first three steps will be cooled with demineralized makeup feedwater and then combined with the remaining condensate streams from subsequent air and water cooling systems. The total stream will then be sent to the gas liquor separator where separation of the tar-oil-naphtha mixture from gas liquor will occur. Gas liquor will be pumped to the gas liquor treatment area and tar oil naphtha mixture will be transported to storage. Vent gas (not shown on Figure 6) is recycled to the gasification area where it is recompressed into the main gas stream.

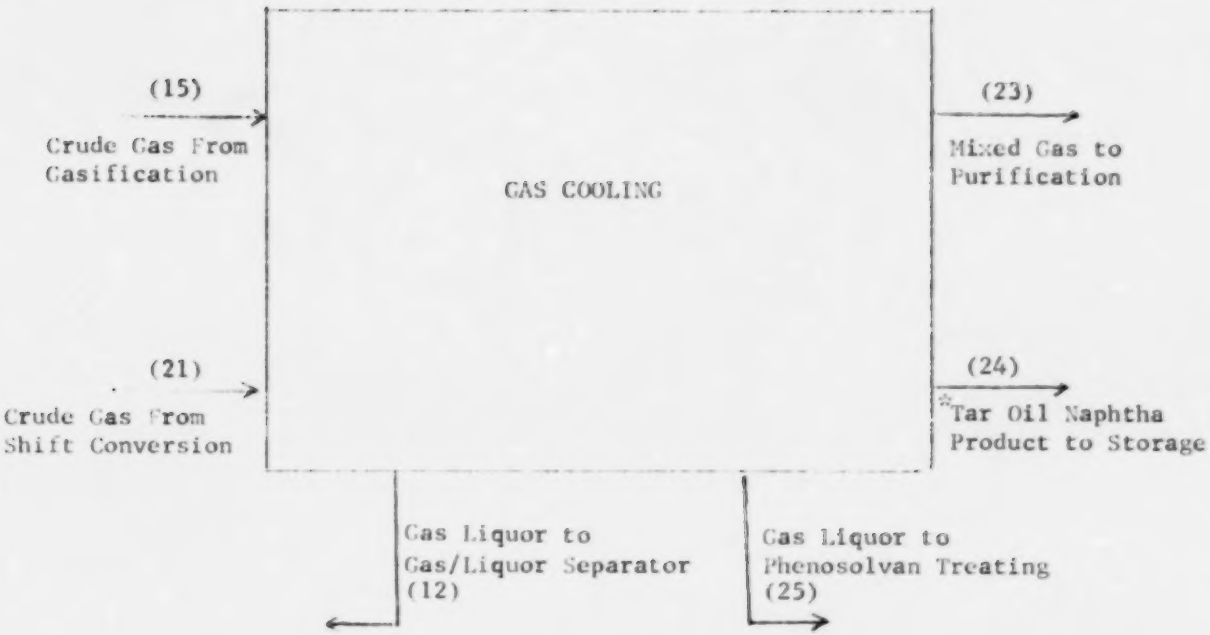


Figure 6

Gas Cooling

Table 6

Gas Cooling

Inlet Streams:

(15) Crude Gas from Gasification; 516 tph dry basis.

(21) Crude Gas from Shift Conversion; 696 tph dry basis.

Outlet Streams:

(12) Gas Liquor to Gas/Liquor Separation.

(23) Mixed cooled gas to Purification; 1225 tph dry basis.

*(24) Tar-Oil-Naphtha Product to Storage; 110 gpm, to be analyzed for trace constituents per Table 18.

(25) Gas Liquor to Phenosolvan Treating.

* Analytical Sample, see Table 18.

3.7 Gas Purification (Figure 7 and Table 7)

The gas purification plant is designed to remove H_2S and COS to a total sulfur concentration of 0.1 vppm (parts per million by volume) before the methane synthesis step. After methanation and first-stage compression, the gas will be washed further to reduce the CO_2 content.

The Lurgi Rectisol Process will be used for gas purification. It is a low-temperature, methanol-wash process.

The mixed gas from the gas cooling area will be chilled before entering the prewash tower, where water and naphtha will be removed by cold methanol wash. Naphtha will be recovered from methanol and water by means of the naphtha extractor. Naphtha recovery will be maximized by recycling the naphtha-methanol mixture through the azeotrope column. The methanol will be recovered by distillation in the methanol-water column. A small water stream (not shown on Figure 7) will be recycled to gas/liquor separation.

The naphtha-free gas will enter the H_2S absorber, where H_2S and COS will be removed down to 0.1 vppm total sulfur by cold methanol wash. Heat of absorption will be removed by refrigeration. Some of the absorbed acid gases will be removed from methanol by multiflash in the flash regenerator. The remaining acid gases will be stripped in the hot regenerator. All the acid gas streams will be combined and delivered to the sulfur recovery plant. Vent gas from the flash regenerator will be recycled to the gasification area for recompression into the main gas stream (not shown on Figure 7).

Upon the recovery of refrigeration, by exchange with inlet gas, the sulfur-free gas will exit the Rectisol Unit for methanation. Following methanation and first-stage compression, the methanation product gas will be returned to the Rectisol Unit where it will again be chilled and will enter the CO_2 absorber. The CO_2 content of the gas will be reduced by the cold methanol wash. The heat of absorption will again be carried away by refrigerant. The high-Btu purified dry gas will be warmed and sent to the second-stage compression unit.

The mechanical compression refrigeration unit will provide refrigeration at two temperature levels. The high-level refrigeration (32 F) will be used to condense most of the water out of the mixed gas and the methanation product gas. The remaining water vapor in the gases will be prevented from freezing by methanol injection. The low-level refrigeration (about -50 F) will be used to achieve the low temperature required for effective methanol wash. The makeup methanol stream for this system is not shown on Figure 7.

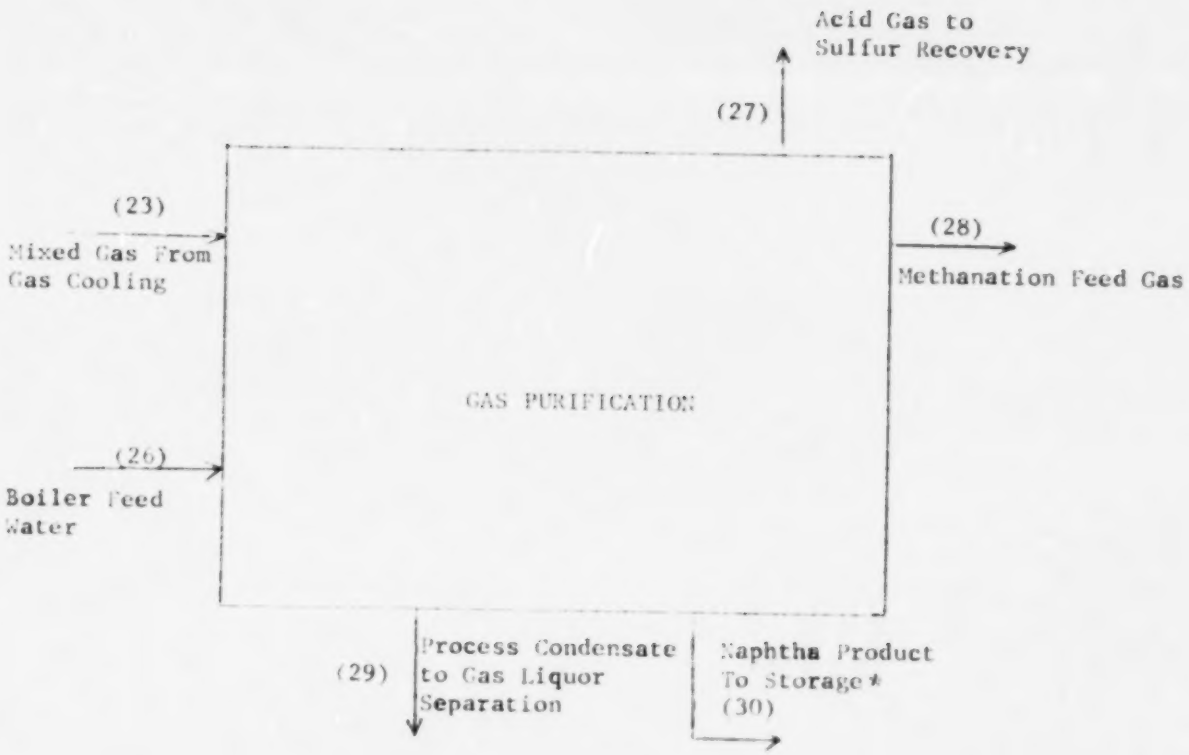


Figure 7

Gas Purification for Lurgi Plant

(Rectisol Plant)

Table 7

Gas Purification for Lurgi Plant

Inlet Streams:

(23) Mixed Gas from Gas Cooling: 1225 tph dry basis.

(26) L.P. Boiler Feed Water; 100,000 pound per hour.

Outlet Streams:

(27) Lean and rich Acid Gases to Sulfur Recovery; 794 tph.

(28) Methanation Feed Gas; 415 tph.

(29) Process Condensate to Gas Liquor Separation.

*(30) Naphtha Product to Storage; 10 tph, to be analyzed per Table 18 for trace constituents.

* Analytical Sample, see Table 18.

3.8 Methane Synthesis (Figure 8 and Table 8)

The methane synthesis area will convert low-Btu synthesis gas to methane-rich, high-Btu gas by the following chemical reactions:

$CO + 3H_2 = CH_4 + H_2O + 94,252$ per pound mole of CH_4 @ 700°F

$CO_2 + 4H_2 = CH_4 + 2H_2O + 77,714$ per pound mole of CH_4 @ 700°F

Both reactions are very exothermic, as indicated by the heats of reaction listed above. Other minor reactions which will take place are the hydrogenation of ethylene to ethane and hydrocracking of ethane to methane.

Fresh feed will be treated for removal of trace sulfur compounds prior to methanation. Fixed-bed downflow reactors employing pelleted reduced nickel catalysts will be used. A synthesis loop, in which process gases are circulated to dilute the concentration of reactants in the feed, will be used to establish operating conditions conducive to equilibrium reactor operations. Reaction heat generated in the synthesis loop will be removed by generating process steam in waste heat boilers. This steam will ultimately be injected into the gasifiers.

A second-stage, one-pass reactor will be used for final cleanup of the gas from the recycle methanation reactor. Methanation product gas from this reactor will be cooled, compressed, and dehydrated before being sent to the gas transmission line.

Feed gas, entering the unit from gas purification, will be heated by exchange with the product gas stream leaving the recycle loop. The hot feed gas will then enter the synthesis loop.

The synthesis loop will be composed of a recycle methanation reactor, waste heat recovery facilities, and a recycle compressor. The feed gas composition to the recycle methanation reactor will be set by combining the fresh feed gas stream with the gas stream circulated by the recycle compressor. Since the reactor has excess catalyst, the reaction will proceed to near equilibrium. Thus, the temperature rise across the reactor can be controlled by setting the concentration of the reactants.

Reaction heat from the recycle methanation reactor will be removed in the waste heat boiler. Preheated boiler feed water will be supplied from gas cooling, with further preheat supplied by cross exchange with the product gas from the cleanup methanation reactor.

Recycle product from the synthesis loop will enter the cleanup methanator where the heating value of the gas will be increased to 954 Btu/scf. Gas leaving the methanator will be cooled by heat exchange with boiler feed water, cross exchange with fresh feed, then with softened water and cooling water. Condensed water will be separated and reused in raw water treatment.

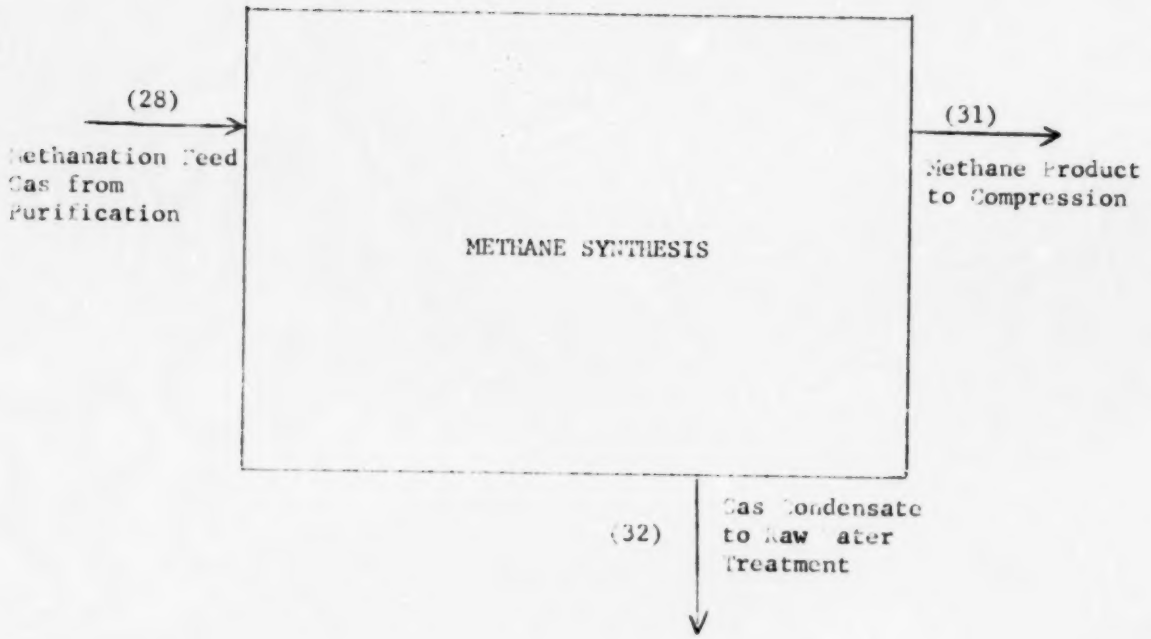


Figure 8

Methane Synthesis

Table 8

Methane Synthesis

Inlet Stream:

(28) Methanation Feed Gas from Purification; 415 tph.

Outlet Streams:

(31) Methane Product to Gas Compression; 257.5 tph.

(32) Gas Condensate to Raw Water Treatment; 157 tph.

3.9 Product Gas Compression and Dehydration (Figure 9 and Table 9)

The product gas compression and dehydration system will consist of two trains of steam turbine-driven compressors, followed by a conventional glycol system for drying the gas. Product gas will be compressed and dried to meet pipeline specifications.

Product gas from methane synthesis will be compressed by means of a multistage centrifugal compressor. Hot gas discharged from the compressor will be cooled with air and cooling water to 90 F. Water condensed in the final aftercooler will be removed before the gas enters the dehydrator. Lean glycol, pumped to the top of the dehydrator, contacts and dries the gas.

Rich glycol from the bottom of the dehydrator will be fed to the glycol regenerator. Heat added to the bottom of the regenerator and reflux added to the top will effect a separation of glycol and water. Lean glycol is pumped back to the dehydrator and the water transferred to the cooling water system for reuse. Glycol makeup to this system is not shown in Figure 9.

Synthetic pipeline gas from the area will flow through a 2.3-mile, 30" pipeline to join El Paso Natural Gas Company's San Juan main line.

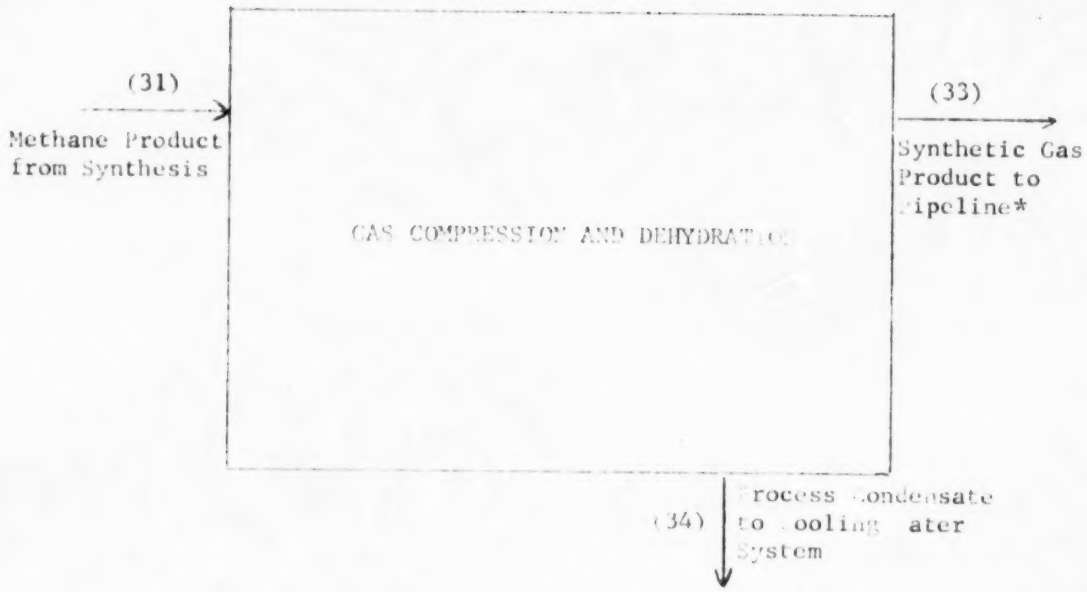


Figure 9

Gas Compression and Dehydration

Table 9

Gas Compression and Dehydration

Inlet Streams:

(31) Methane Product from Synthesis; 257.5 tph.

Outlet Streams:

*(33) Synthetic Gas Product to Pipeline; 256.9 tph. To be analyzed for trace constituents per Table 18.

(34) Process Condensate to Cooling Water System; 715 pounds per hour.

* Analytical Sample.

3.10 Sulfur Recovery (Figure 10 and Table 10)

The Stretford process will be used to recover elemental sulfur from hydrogen sulfide present in the acid gas streams. This Stretford unit will operate at about 10 psig. A pressure Stretford absorber operating at about 250 psig will similarly remove hydrogen sulfide from low-Btu fuel gas in the fuel-gas treatment area.

Hydrogen sulfide will be removed by the Stretford solution. The solution will then be regenerated by contact with air.

The overall reaction can be summarized as follows:

$$2H_2S + O_2 = 2H_2O + 2S$$

Hydrogen sulfide content in the gases from the Stretford unit will be 10 ppm or less by volume. The carbonyl sulfide (COS) content will not be significantly reduced by contact with Stretford solution.

The absorption section of the plant will consist of two trains for treating the lean H_2S acid gases and a single train for the rich H_2S acid gas. A single oxidizer section will serve to regenerate the Stretford solution from the absorbers in both the low- and high-pressure units.

Feed to the lean H_2S absorbers will be a combined stream consisting of acid gas streams and expansion gas. Feed to the rich H_2S adsorber will be the rich H_2S acid gas stream from gas purification and the coal lock gas stream. Gases fed to the bottom of the absorber towers will be contacted countercurrently by the Stretford solution fed to the top. The lower part of the absorbers will act as a hold tank for the completion of chemical reactions between hydrogen sulfide and the Stretford solution.

Off-gas from the top of the lean H_2S absorbers will be primarily CO_2, but will contain about 10 ppm by volume of hydrogen sulfide and any residual sulfur compounds (such as COS) not converted in the process. The stream, combined with the oxidizer off-gas, will be vented to the atmosphere. Off-gas from the rich H_2S absorber will be incinerated.

Rich solution from the absorbers will be combined with solution from the fuel-gas treating area and flow to the oxidizer. Air will be blown in at the bottom, and sulfur froth will be floated to the surface. The sulfur froth will be pumped to the sulfur separator. Sulfur will be removed from the separator as a liquid and accumulated in a storage pit.

The regenerated Stretford solution will flow from the oxidizer to the pumping tank. Lean solution will be pumped back to the top of the absorbers and to the fuel-gas treating area.

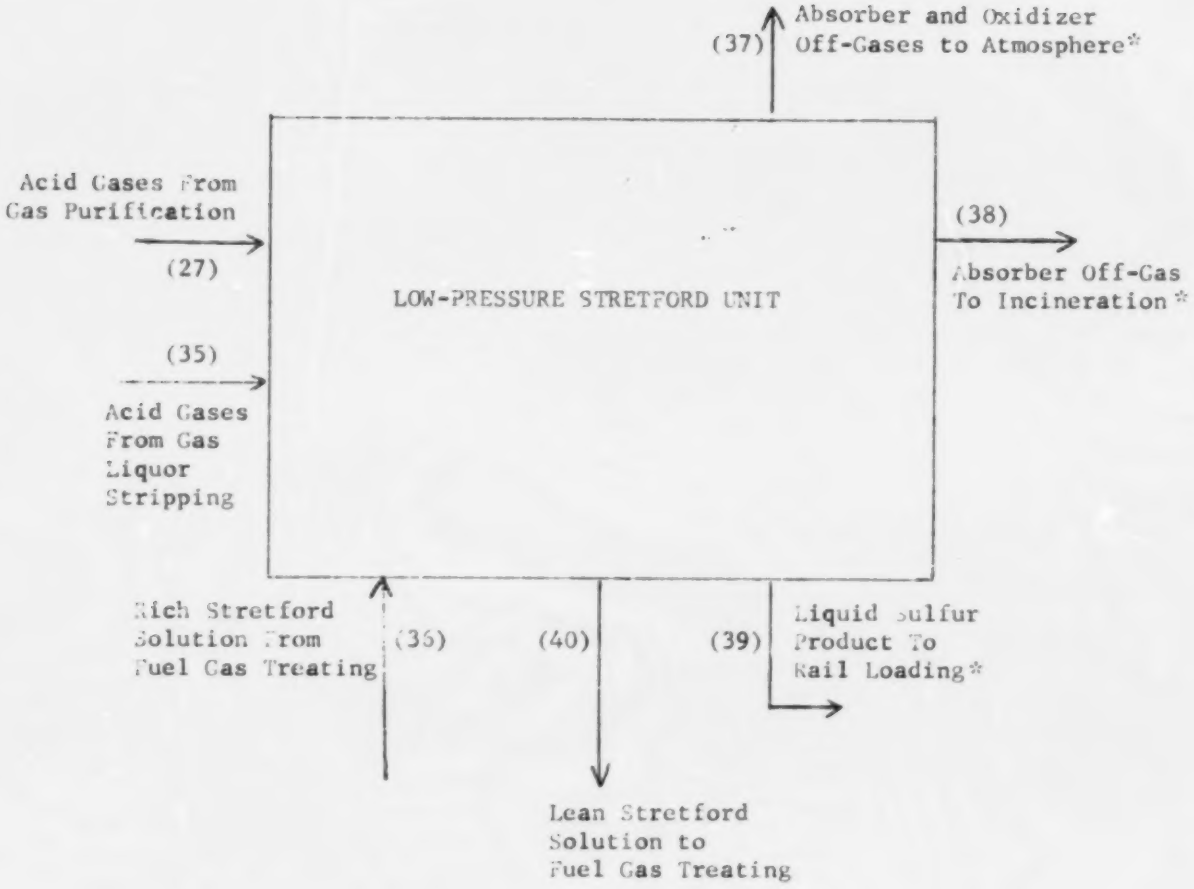


Figure 10

Sulfur Recovery for Lurgi Plant

Table 10

Sulfur Recovery

Inlet Streams:

(27) Acid Gas from Gas Purification; 794 tph.

(35) Acid Gas from Gas Liquor Stripping; 9 tph.

(36) Rich Stretford solution from Fuel Gas Treating.

Outlet Streams:

*(37) Absorber and Oxidizer Off-Gas to Atmosphere; 900 tph. To be analyzed for sulfur compounds and trace constituents per Table 18.

*(38) Absorber Off-Gas to Incineration; 23.8 tph. Incinerator stack to be analyzed per Table 18.

*(39) Liquid Sulfur Product to Rail Loading; 7.8 tph. To be analyzed for trace constituents per Table 18.

(40) Lean Stretford solution to Fuel Gas Treating.

* Analytical Samples.

3.11 Gas Liquor Treatment (Figure 11 and Table 11)

The gas liquor treatment area is designed to remove ammonia and phenol from contaminated water effluents. The phenol will be recovered as a byproduct, and the ammonia will be recovered in aqueous solution.

In the latest design, the gas liquor treatment area has been broken down into sub-sections which are phenol extraction and gas liquor stripping sub-sections.

The phenol extraction area is designed to remove phenols from the clarified gas liquors. Two parallel systems are provided for gas liquor filtration and extraction, one each for contaminated and clean gas liquors. Common solvent recovery and crude phenol-solvent separation equipment is provided.

The Lurgi Phenosolvan process will be used to remove and recover phenols from the clarified gas liquor.

The following paragraph applies to both the contaminated and clean gas liquor systems. Gas liquor will contain phenols, ammonia, carbon dioxide and hydrogen sulfide. Incoming gas liquor will first pass through gravel filters for removal of suspended matter, and then through the extractors where an organic solvent will extract the phenols (forming the extract phase). The dephenolized gas liquor (raffinate) will then be pumped to gas liquor stripping, where traces of solvent will be removed by nitrogen stripping. The nitrogen stream, which comes from the oxygen production area, is not shown on Figure 11.

The phenol-rich extracts will flow to the solvent distillation column. Heat applied to the column will drive most of the solvent overhead. Vapors from the tower will be condensed and the solvent recycled to the extractors. Fresh solvent makeup will be added to the recycle solvent stream. A water-phenol solution will be recovered from the bottom of the solvent distillation column. This material will be combined with phenol from the bottom of the solvent recovery scrubber and fed to the solvent recovery stripper. There, heat will be applied to strip the solvent and water overhead for recycle to the solvent distillation column. A crude phenol product will be recovered from the bottom of the stripper and transferred to storage and loading.

Solvent-rich nitrogen from stripping dephenolized gas liquor will be returned and contacted with crude phenols to remove the solvent. Scrubbed nitrogen from the solvent recovery scrubber will be returned to gas liquor stripping, where the stream will be contacted with filtered gas liquor to remove traces of phenols. A phenol-rich gas liquor stream will be returned upstream of the extractors.

The gas liquor stripping area is designed to remove solvent, ammonia, carbon dioxide, and hydrogen sulfide from the dephenolized gas liquors. A separate solvent stripper will be provided for the dephenolized contaminated gas liquor. A single train, except for two ammonia strippers, will be used for the dephenolized clean gas liquor.

The incoming gas liquors will be separately introduced to solvent strippers where nitrogen will be used to strip out traces of solvent picked up in the extraction steps. The solvent-rich nitrogen streams will be combined for solvent recovery and returned. Makeup nitrogen will be added to the returned gas and the combined stream will then be compressed, washed with gas liquor to remove traces of phenol, and recycled through the solvent stripper.

Solvent-free, contaminated liquor from the solvent stripper will be sent to ash disposal. Solvent-free, clean gas liquor leaving the solvent stripper will be heated in the deacidifier to remove dissolved carbon dioxide and hydrogen sulfide. Acid gases driven off overhead will be sent to sulfur recovery.

Ammonia removed from the clean gas liquor by steam stripping in the ammonia stripper will be collected overhead as an ammonia solution of about 20 weight percent. Waste liquor from the ammonia stripper will be used directly for cooling tower makeup.

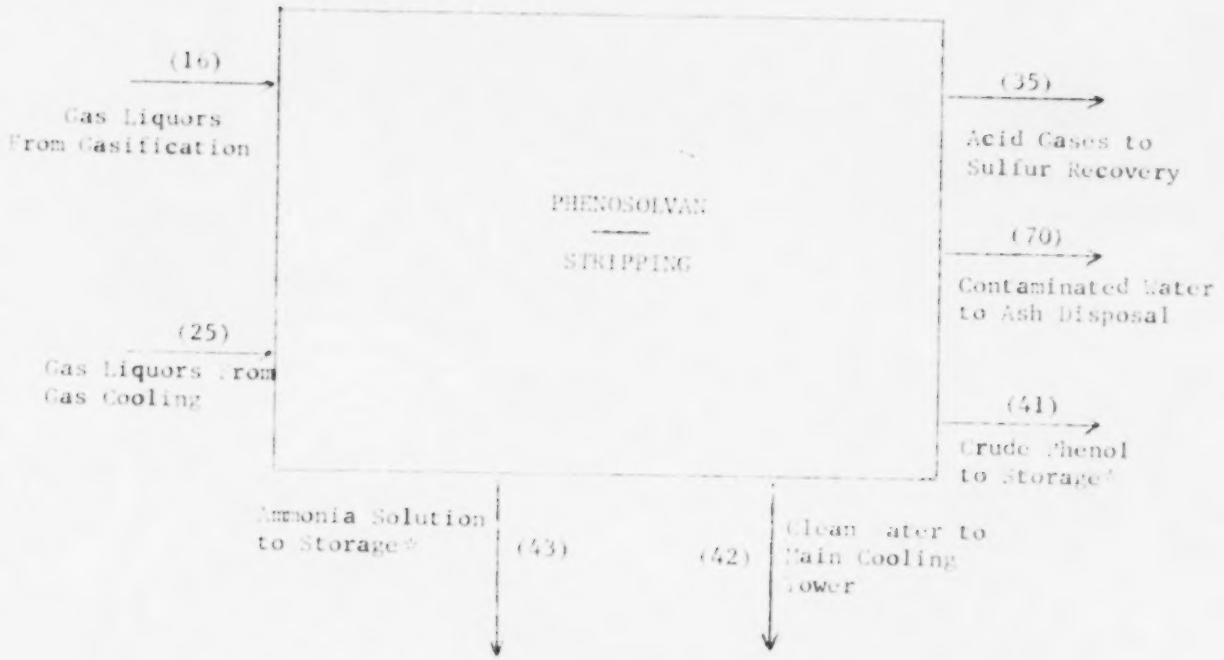


Figure 11

Gas Liquor Treatment

Table 11

Gas Liquor Treatment

Inlet Streams:

(16) Gas Liquors from Gasification/Separation.

(25) Gas Liquors from Gas Cooling.

Outlet Streams:

(35) Acid Gases to Sulfur Recovery; 9 tph.

(70) Contaminated Water to Ash Disposal; 82 tph.

*(41) Crude Phenol to Storage; 5.6 tph. To be analyzed for trace constituents per Table 18.

(42) Clean Water to Main Cooling Tower; 600 tph.

*(43) Ammonia Solution to Storage; 53.6 tph. To be analyzed for trace constituents per Table 18.

* Analytical Samples.

3.12 Fuel Gas Production and Cooling
(Figure 12 and Table 12)

Basic design for the fuel-gas production area is provided by Lurgi. Navajo coal will be gasified in airblown Lurgi gasifiers operating at about 385 psig.

Sized coal will be conveyed from coal preparation to coal bunkers located above the gasifiers. The coal will be fed to the gasifiers through coal locks which will be pressurized by a slip stream of lock-filling gas. The Lurgi gasifiers are water-jacketed vessels. Hot compressed air and process steam will be mixed and introduced into the gasifiers. Ash will be removed from the bottom of the gasifiers through ash locks and transported to ash disposal.

Hot crude gas leaving the gasifiers will be cooled rapidly by quenching with a gas liquor spray in wash coolers. Crude gas from the wash coolers will be further cooled in waste heat boilers to produce 15 psig steam. A purge stream of tarry gas liquor will be drawn off to gas liquor separation. Recycle gas liquor will be injected into the wash cooler as makeup. Boiler feed water and recycle gas liquor streams are not shown on Figure 12.

Crude fuel gas from this area flows to fuel gas cooling. The fuel gas cooling area is designed to cool the hot crude fuel gases to near ambient temperature.

Crude fuel gas will first be cooled by aerial coolers. Final cooling of the crude fuel gas will be by cooling water. Oily gas liquor condensed in both cooling steps will be combined and sent to gas liquor separation.

Cooled fuel gas will be sent to fuel gas treating.

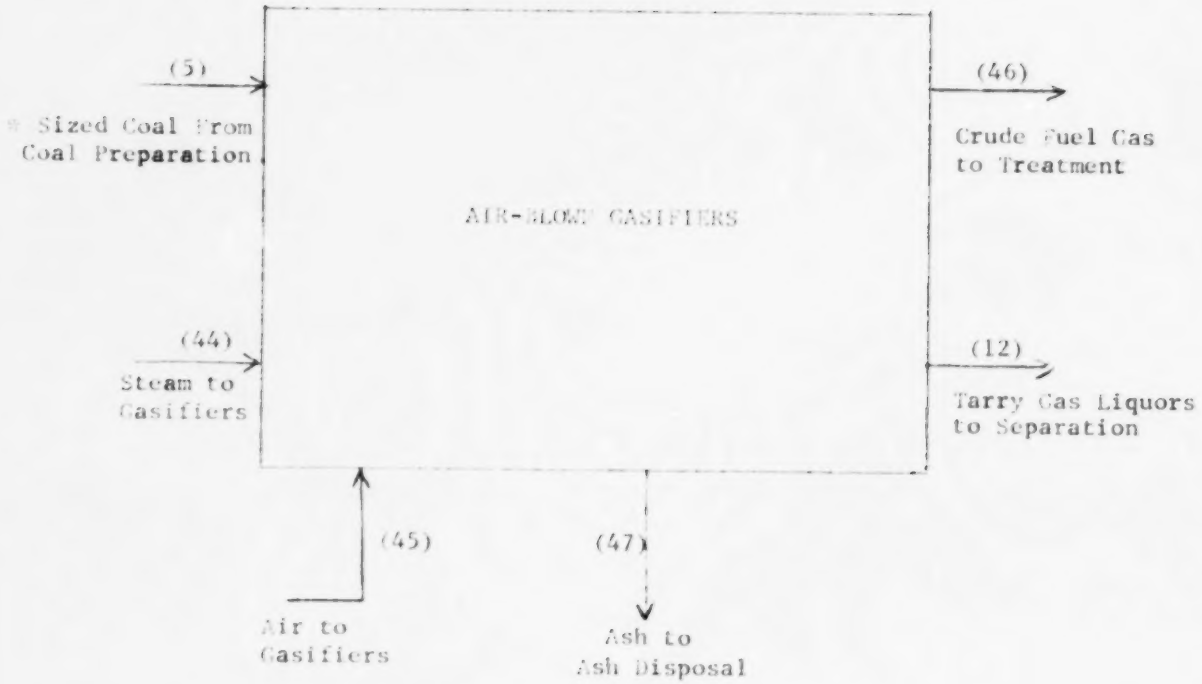


Figure 12

Fuel Gas Production

Table 12

Fuel Gas Production

Inlet Streams:

*(5) Sized coal from Coal Preparation; 208 tph.

(44) Steam to Gasifiers; 150 tph.

(45) Air to Gasifiers; 266 tph.

Outlet Streams:

(12) Tarry Gas Liquors to Gas Liquor Separation.

(46) Crude Fuel Gas to Fuel Gas Treatment; 444 tph.

(47) Ash to Ash Disposal; 42 tph.

* Analytical Sample.

3.13 Fuel Gas Treating (Figure 13 and Table 13)

The fuel gas treating area is designed to clean fuel gas by treating with the Stretford process. This Stretford process will operate at about 250 psig in contrast to the 10 psig operating pressure for the main Stretford unit. Hydrogen sulfide will be removed by the Stretford solution. The solution will then be regenerated by contact with air. Overall, the reaction can be summarized as follows:

$$2H_2S + O_2 = 2H_2O + 2S$$

Hydrogen sulfide content in the gases will be less than 10 vppm. Carbonyl sulfide (COS) content of the fuel gas will not be significantly reduced by contact with the Stretford solution.

A single oxidizer section located in the sulfur recovery area will serve to regenerate the rich Stretford solution from the absorbers in this section.

Crude fuel gas is fed to the bottom of a contactor tower and washed countercurrently with lean Stretford solution fed into the top. The lower part of the absorber and the digester vessel downstream will act as a hold tank for the completion of chemical reactions between hydrogen sulfide and the Stretford solution.

Lean solution from the sulfur recovery area will be pumped to the contactor. Energy will be extracted from the rich solution leaving the digester by depressurizing the solution through a power recovery turbine coupled to the booster pump. Rich solution will be transferred to the sulfur recovery area for regeneration.

A portion of the treated fuel gas at near ambient temperature and about 250 psig will be used to fire gas turbines in steam and power generation. The balance of the stream will flow to gas compression where the fuel gas will be heated and expanded to recover power, and then be used to fire heaters and boilers.

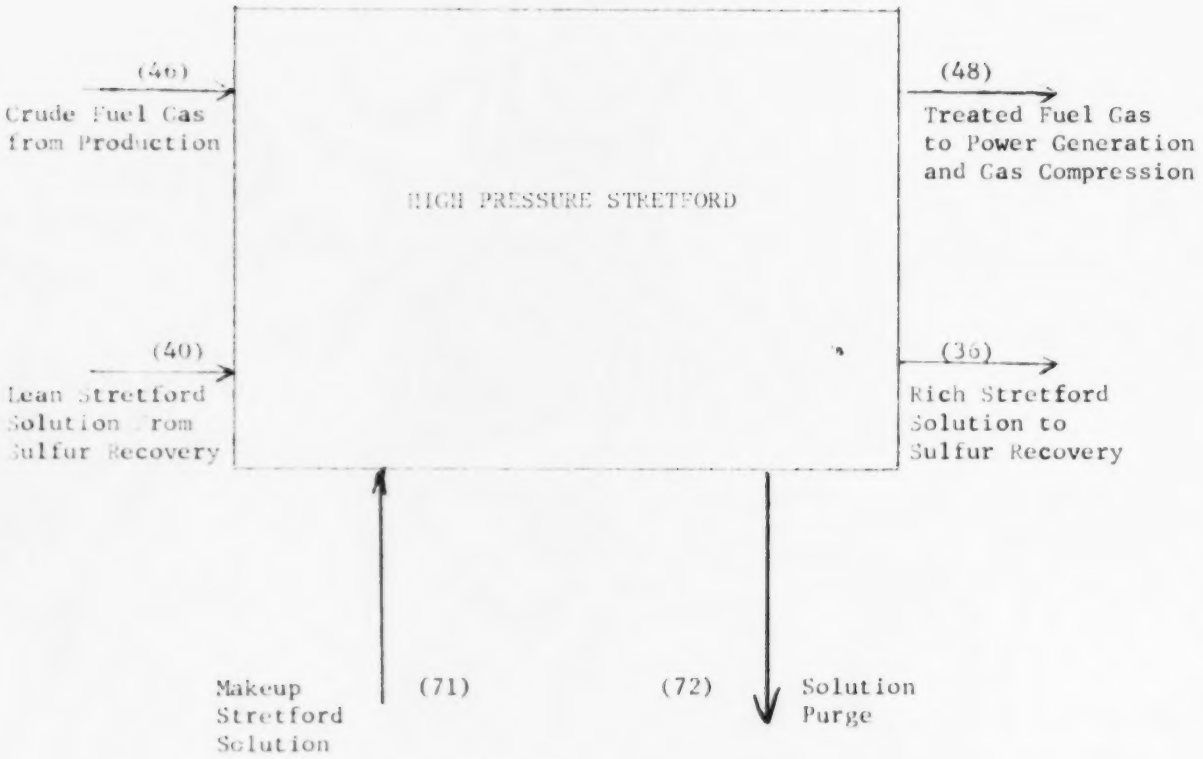


Figure 13

Fuel Gas Treating

Table 13

Fuel Gas Treating

Inlet Streams:

(40) Lean Stretford Solution from Sulfur Recovery.

(46) Crude Fuel Gas from Production; 444 tph.

(71) Makeup Stretford Solution (Quantity not specified).

Outlet Streams:

(36) Rich Stretford Solution to Sulfur Recovery.

(48) Treated Fuel Gas to Power Generation; 443 tph.

(72) Solution Purge (Quantity not defined).

3.14 Steam and Power Generation (Figure 14 and Table 14)

Power generation will be from four gas turbine driven generator sets. The capacity of each generator is 33% of normal plant requirements. Excess capacity is to assure continuous, full-load operation with one unit removed from service for inspection or repair.

Steam generation will consist of a combination of process waste heat boilers and heat recovery boilers on gas turbine exhaust. Generally, low pressure steam from the process waste heat boilers will supply process heat requirements, and high-pressure steam will provide process reaction steam and motive power steam.

Eight gas-turbine, heat-recovery boilers will be provided; four on power generation turbines and four on air compression turbines. Excess capacity in the form of one spare electrical generator train plus a free standing boiler will provide flexibility in meeting peak demands and will assure continuous full-load operation whenever one unit is shutdown for inspection or repair.

Steam generated at 612 psia in the methane synthesis area will be superheated to provide motive power steam and process reaction steam to the coal gasifiers.

Hot exhaust gases from the gas turbines will be utilized in heat recovery boilers to generate 1150 psig superheated steam. The boilers will be supplemental fire as required to maintain proper steam conditions. The standing boiler will be fuel gas-fired to generate 1150 psig superheated steam in emergency situations, for startups, and for flexibility.

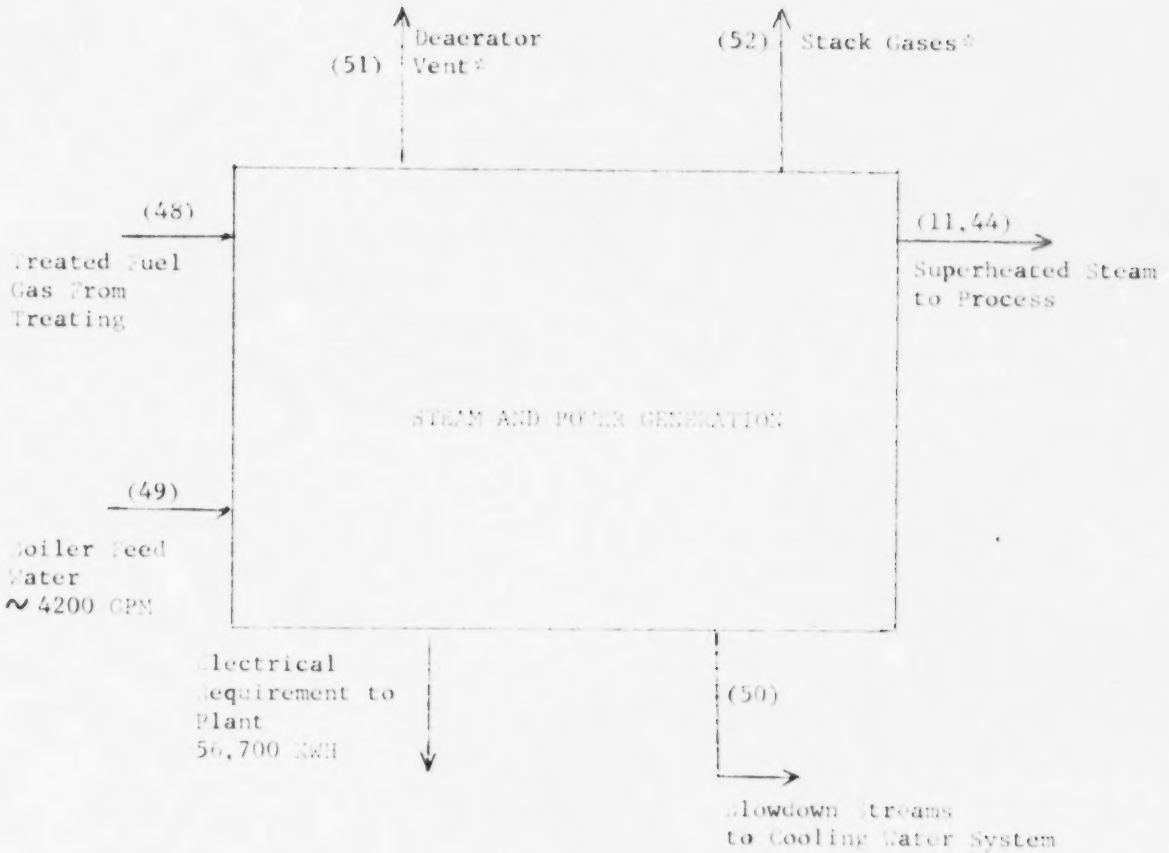


Figure 14

Steam and Power Generation

Table 14

Steam and Power Generation for Lurgi Plant

Inlet Streams:

(48) Treated Fuel Gas; 443 tph.

(49) Boiler Feed Water; ~4200 GPM.

Outlet Streams:

(11)+(44) Superheated Steam at 1150 and 550 psig and Saturated Steam at 15 psig to process; ~4100 GPM.

(50) Boiler Blowdown to Cooling Water System; 60 GPM.

*(51) Deacrator Vent to Atmosphere; ~40 GPM. To be analyzed for trace constituents per Table 18.

*(52) Stack Flue Gases to Atmosphere. To be analyzed per Table 18 as stack gases.

* Analytical Samples.

3.15 Raw Water Treating (Figure 15 and Table 15)

The raw water treating system will receive approximately 6000 gpm of raw water and 600 gpm of process condensate. About 2300 gpm of zeolite softened water for makeup to the low-pressure steam generation systems and 2200 gpm of demineralized water for boiler feedwater and gasifier jacket water will be produced. In addition, an average of 20 gpm of potable water for the plant's domestic water users, 129 gpm for general plant utility water system, and about 440 gpm of treated water for cooling tower makeup will also be produced. Condensate returns from the plant will be collected and treated to remove trace hydrocarbon contaminants before being utilized as makeup to the high-pressure steam generation systems. The hydrocarbon removal system has not been detailed, nor has the disposition of separated hydrocarbon been indicated.

Raw water will be pumped from the raw water reservoir to a lime softener-clarifier for chemical treatment. Pebbled quicklime will be unloaded pneumatically and conveyed to a storage silo. Lime slaking systems will provide a lime feed to the clarifier. Alum feeder and polymer feeder systems will provide other necessary water treating chemicals to the clarifier. Treated water from the clarifier will drain to a clearwell which gives a brief storage time. From the clearwell the water will be pumped through anthracite-filled gravity filters. The filtered water will then flow through either demineralizer sets or zeolite softener sets and then on to the steam generation areas.

Process condensate will be airblown to strip dissolved light hydrocarbon gases and carbon dioxide before being combined with the zeolite softener effluent.

A small stream of treated water will be chlorinated and piped to an elevated potable water tank. The plant potable water system will then be supplied from this tank by gravity.

Tankage for the water systems will be as follows:

a.	Treated Water	(2)	2,500,000 Gallon Tanks
b.	Demineralized Water	(2)	200,000 Gallon Tanks
c.	Softened Water	(2)	750,000 Gallon Tanks
d.	Condensate	(2)	1,100,000 Gallon Tanks

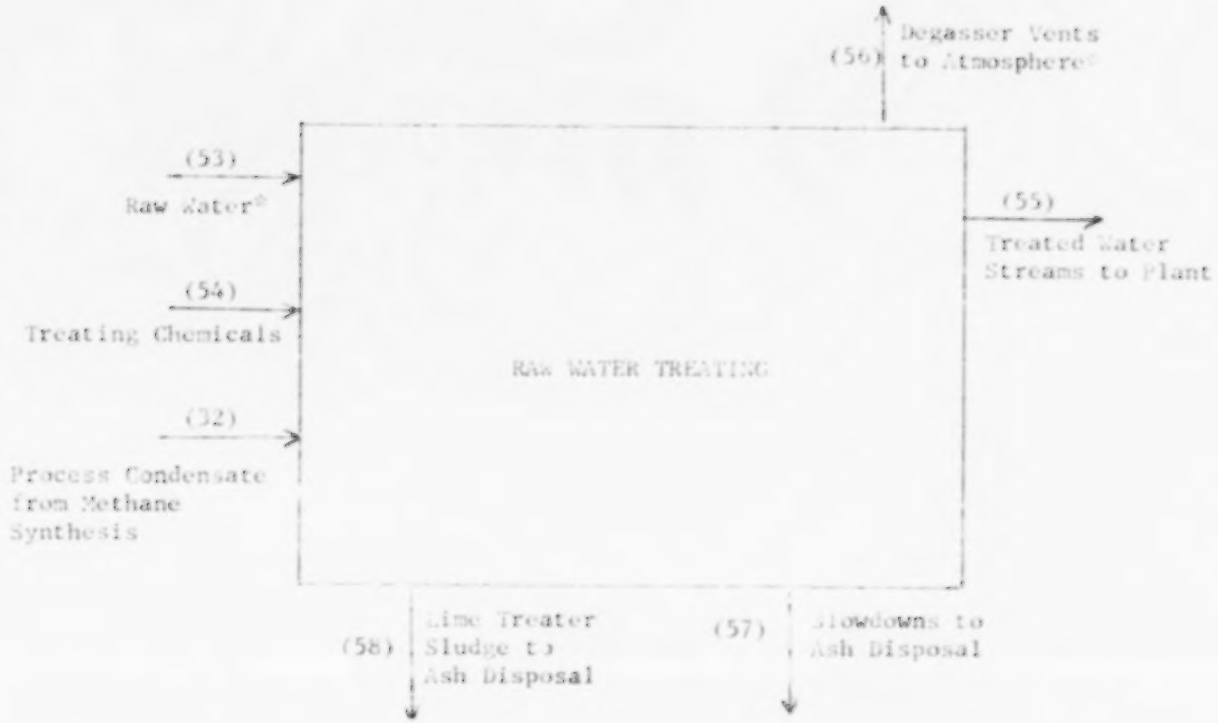

(56) Degasser Vents to Atmosphere*
(53) Raw Water*
(54) Treating Chemicals
(52) Process Condensate from Methane Synthesis
RAW WATER TREATING
(55) Treated Water Streams to Plant
(58) Lime Treater Sludge to Ash Disposal
(57) Slowdowns to Ash Disposal

Figure 15

Raw Water Treating

Table 15

Raw Water Treating

Inlet Streams:

(32) Process Condensate From Methane Synthesis; 157 tph.

*(53) Raw Water; 6000 gpm. To be analyzed as water sample per Table 18.

(54) Water Treatment chemicals, including pebbled quicklime, sodium hydroxide solution, sulfuric acid, alum, polymer solution, chlorine, hypochlorite, demineralizer and zeolite polymers, salt, anthracite filter media.

Outlet Streams:

(55) Treated Water to Plant.

*(56) Vent from condensate degasser to atmosphere; 35 gpm. To be analyzed for trace constituents per Table 18.

(57) Blowdowns to Ash Disposal; 270 gpm.

(58) Lime Treater Sludge to Ash Disposal; 220 gpm.

* Analytical Samples.

3.16 Cooling Water System (Figure 16 and Table 16)

Two separate cooling water systems will be provided for the complex: (1) a clean water system which will be dedicated exclusively to the cooling of pure oxygen streams, and (2) the main system which will be for the remaining cooling loads within the complex. Both systems will be designed to produce 75 F cooling water.

The clean water system will consist of one two-cell, cross-flow tower designed to reject 62 million Btu per hour at a circulation rate of 8200 gpm. The main cooling water system will consist of three five-cell cross-flow towers designed to reject 1144 million BTU per hour at a circulation rate of about 153,000 gpm.

The clean cooling water system will be supplied from one two-cell cooling tower. Each cell will be rated at 31 million Btu per hour. The tower will be equipped with three vertical turbine pumps mounted in the pump pit, with one pump acting as a spare. Makeup water to the clean water system will be blowdowns from the process waste heat and power boilers. Total flow available for makeup will be about 460 gpm. Cold water will leave the tower at 75 F and return at 90 F. Blowdown from the clean cooling tower will be used as part of the makeup for the main cooling tower.

The main cooling water system will be supplied from three five-cell cooling towers. Each cell will be rated at 76 million BTU per hour. The cooling towers will be erected over a concrete basin with a pump pit to the side. Each tower will be equipped with four vertical turbine pumps mounted in the pump pit, with one pump acting as a spare. The main source of makeup water, approximately 2400 gpm, will be supplied from gas liquor stripping. Other makeup streams include about 440 gpm of treated water, about 250 gpm of blowdown from the clean cooling water system, and 20 gpm of treated sewage. Cold water will leave the tower at 75 F and return at 90 F.

Water treating chemicals will be added to both water systems as required to control corrosion, scale formation, plant growth, and pH. Sidestream filtration will be used to control the suspended solids.

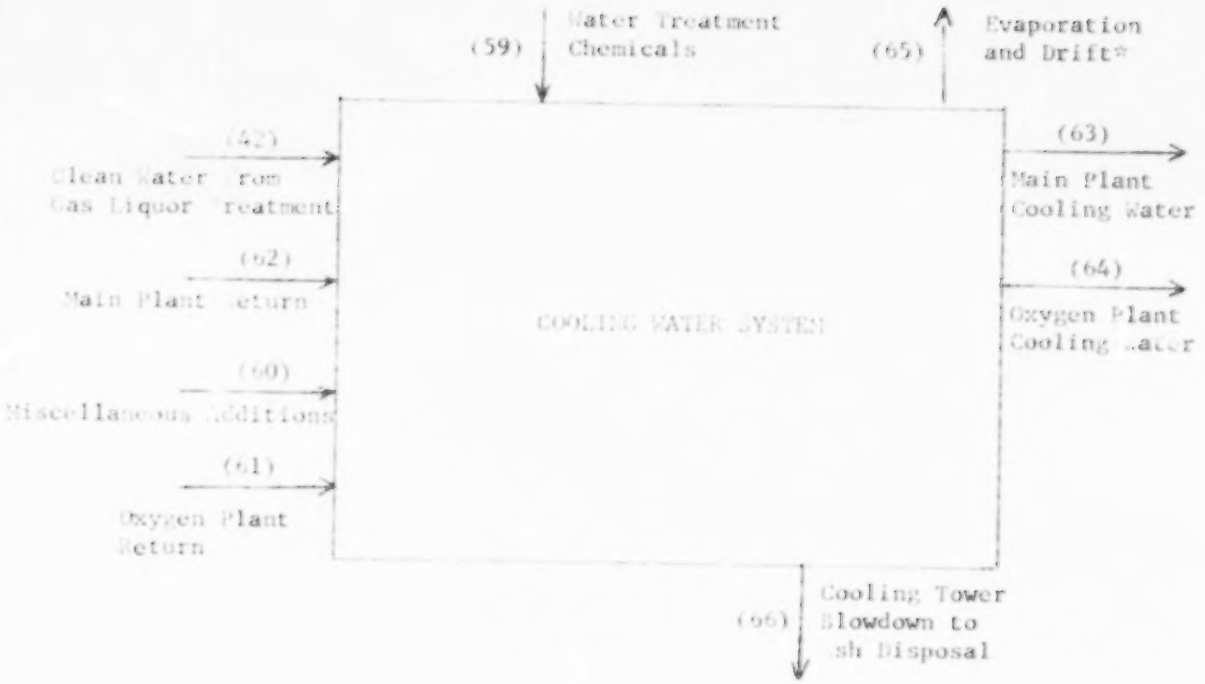


Figure 16

Cooling Water System

Table 16

Cooling Water System

Inlet Streams:

(42) Clean Water from Gas Liquor Treatment; 2400 gpm.

(59) Water Treatment Chemicals including anti-foam package, biological (growth control) package, inhibitor feed package, pH (sulfuric acid) package.

(50)+(60) Miscellaneous Blowdowns and Treated Water Additions; 920 gpm.

(61) Oxygen Plant Return; 8200 gpm.

(62) Main Plant Return; 153,000 gpm.

Outlet Streams:

(63) Main Plant Cooling Water Requirement; 153,000 gpm.

(64) Oxygen Plant Cooling Water Requirement; 8200 gpm.

(65) Evaporation from Towers; 2800 gpm and Drift from Towers; 160 gpm. Atmosphere downwind of towers to be analyzed for trace constituents per Table 18.

(66) Blowdown from Cooling Water System to Ash Disposal; 330 gpm.

Analytical Sample.

3.17 Ash Disposal (Figure 17 and Table 17)

Wet ash facilities will be designed to handle all of the ash discharged from the airblown and oxygen-blown gasifiers. The equipment will be adequately designed to allow for maximum anticipated variations in ash rate. Coarse ash will be trucked to the mine and fine ash will be stored in a pond.

The ash facilities at the mine and gasification area are interconnected by a continuous belt conveyor.

Ash will be discharged dry and hot from the individual gasifier ash locks into a sluiceway. Water flowing in the launder will quench and transfer the ash to classification and dewatering equipment. The coarse dewatered ash will be transferred on a belt conveyor to the mine ash handling area for disposal in the mine.

The fine ash from the classification step will be dewatered in a thickener and pumped to a fine ash pond for disposal. Water from the thickener will be reclaimed and recycled to the sluiceway. Excess water in the system will be bled to evaporation ponds for disposal.

Figure 17

Ash Disposal

Table 17

Ash Disposal

Inlet Streams:

(18) Dry Ash from Main Gasifiers; 190 tph.

(39) Contaminated Gas Liquor; 330 gpm.

(47) Dry Ash from Fuel Gas Production; 42 tph.

(57) Blowdown from Raw Water Treating; 270 gpm.

(58) Lime Treated Sludge from Raw Water Treating, 220 gpm.

(66) Cooling Tower Blowdown; 330 gpm.

Outlet Streams:

*(67) Wet Ash to Mine; 280 tph. To be analyzed for trace constituents per Table 18.

*(68) Separated Water to Evaporation Ponds; 900 gpm. To be analyzed for trace constituents per Table 18. Atmosphere over evaporation ponds to be analyzed per Table 18.

*(69) Wet Fine Ash Slurry to Fine Ash Pond; 150 gpm. To be analyzed for trace constituents per Table 18. Atmosphere over evaporation ponds to be analyzed per Table 18.

* Analytical Samples.

3.18 Process Analytical Summary

The streams indicated for analysis around the Lurgi Process model are summarized in Table 18, along with specific references to suggested sampling and analytical procedures described in the Analytical Sections 5-9. Table 19 shows constituents present in coal feeds to gasification for SNG and fuel gas production.

The gasification system as described herein will almost certainly be modified appreciably before commercialization. The analyst is urged to adapt the logic of this analytical scheme to his specific requirements.

It is almost certain that existing legal sanctions will have increased by the time coal gasification systems are commercialized in this country. The analyst may be required to extend the list of analyses, although we have attempted to anticipate some future requirements. For example, polynuclear aromatic (PNA) materials, which may exhibit carcinogenic properties (31,32), may be present in almost any of the effluent streams from this system, and may also constitute significant fractions of the coal liquid byproducts. We have not indicated that all streams be analzyed for PNA, although this may be a future requirement. Similarly, we have not indicated that the coal liquid products be so analyzed, even though they will certainly contain harmful PNA, since the potential hazards of such materials are recognized within the industrial sector which now manufactures and utilizes coal-derived byproducts.

We have not always indicated that particulates recovered from gas or atmospheric samples be completely analyzed. The composition of coal dust, for example, should approximate the feed coal composition. However, procedures for determining the ultimate composition of particulate samples is included in the Analytical Sections. Future restrictions may require such definition. Moreover, it will be possible to analyze any stream in a given sample class for any of the components for which analytical procedures are indicated, so that the analyst may readily expand the analytical system to meet anticipated requirements.

We have attempted to indicate that all heater, incinerator, and boiler stack effluents shall be analyzed, even though such heaters may not have been specifically designated in the process scheme. Table 20 shows constituents expected in flue gases from boiler and heater stacks. Similarly, we intend that the atmosphere in the vicinity of all storage tankage or open storage areas, water cooling towers, and over all holding and evaporation ponds be analyzed for free hydrocarbons. The particular location and plant layout, prevailing winds, and climate will be taken into consideration in the sampling scheme.

This plant will generate additional long-term residuals not detailed in the processing sequence, including spent catalysts (from shift conversion and methanation) and spent filter media. Although such materials may be expected to be sulfated in general, and to contain other polluting materials when discharged, the quantities involved should not significantly affect overall long-term plant balances, unless the expected turnover period is shortened due to malfunction or emergency. Analysis of such discharged streams is indicated, however, to ascertain downstream pollution potential, since such materials will probably be buried with ash in this case unless metal values justify reclamation or unless future sanctions forbid such disposition. Very little attention has so far been given to the "neutralization" of such materials from other industrial processing.

We note also that it is necessary to chemically clean the boilers and associated piping in the power plant before these facilities are placed in operation, and at intervals of 2-3 years thereafter (40). Other plant facilities may require similar treatment. Both acidic and alkaline solutions are used in chemical cleaning. The acidic wastes would typically consist of solutions of hydroxyacetic and formic acids, or hydrochloric acid, at concentrations of less than 5%. The alkaline wastes would typically consist of dilute sodium phosphate solutions (less than 1%). A large amount of water would have to be used for flushing the system.

For a boiler of the size indicated, the total amount of waste produced could amount to several hundred thousand gallons of acidic and alkaline solutions, and up to a million gallons of flushing water. In this case, these wastes may be routed to settling ponds or to the ash basins, where they may be diluted or neutralized.

Finally, although not included in the process scheme herein presented, potential pollution from mining areas and from associated ash disposal operations are additional aspects that will concern any process developer and the immediate population, including plant operators, which may be affected. Environmental guidelines for water discharges from mining facilities already exist (43), and it is probable that future relevant solid waste restrictions will be promulgated.

Table 18

Summary of Effluent Streams to be Analyzed for Lurgi Plant

COAL GASIFICATION

LURGI PROCESS MODEL

Stream No.	Stream Name	Analysis For	Analytical Section Reference
4	Dust and Fumes in Coal Preparation Area	Atmosphere in enclosed spaces, discrete stack emissions from enclosed spaces and from dust collection equipment, and atmosphere in vicinity of coal piles, open conveying and handling equipment, and coal fines collection system to be analyzed for particulates.	Total particulates to be determined in enclosed spaces using a high volume sampler, Section 9; in stacks using EPA Method No. 5, Section 9; and the ASTM D 1739 dust fall test will be performed at various site locations.
5	Sized Coal to Gasifiers and to Fuel Production (See Tables 1 and 19)	Complete coal analysis including trace elements.	Coal will be analyzed for the elements listed in Section 7, Table VI and will be analyzed to determine its gross composition as indicated in Section 7, Table VII.
17	Coal Tar Product*	Trace Sulfur Compounds Trace Elements	Tar will be analyzed for total sulfur (Section 8, Table X); and the trace elements listed in Section 8, Table VIII will be measured.
22	Shift Startup Heater Stack Gas	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO_2/SO_3, NO_x, CO, CO_2, COS, H_2S, and CH_3SH and for particulates. Refer to Section 9.
24	Tar-Oil-Naphtha Product*	Sulfur Trace Elements	This stream will be analyzed for the metals listed in Section 8, Table VIII and for total sulfur as indicated in Section 8, Table X.
30	Naphtha Product*	Sulfur Trace Elements	This stream will be analyzed for the metals listed in Section 8, Table VIII and for total sulfur as indicated in Section 8, Table X.

Table 18 (Cont'd)

Summary of Effluent Streams to be Analyzed for Lurgi Plant

COAL GASIFICATION

LURGI PROCESS MODEL

Stream No.	Stream Name	Analysis For	Analytical Section Reference
33	Synthetic Gas Product	Trace Sulfur Compounds Metal Carbonyls	The gas will be analyzed for particulates, COS, H_2S, CH_3SH and SO_2/SO_3; and for iron, nickel, & dicobalt carbonyls. Refer to Section 9.
37 38	Absorber and Oxidizer Off-Gases and Incinerator Stack Gases	Trace Sulfur Compounds Particulates (V, Na)	Off-gases to be analyzed for particulates and for COS, H_2S, CH_3SH and SO_2/SO_3, see Section 9. In addition Na and V will be determined on particulates, see Section 7.
39	Liquid Sulfur Product	Trace Elements	Sulfur will be analyzed for the metals listed in Section 8, Table VIII, by adaptation of methods which were designed for oil analysis.
41	Crude Phenol Product	Total Sulfur Trace Elements	The trace elements in Section 8, Table VIII will be determined, and the sulfur content will be determined.
43	Aqueous Ammonia Solution Product	Trace Sulfur Compounds Trace Elements	Sulfide, thiocyanate, and sulfite will be measured, Section 6, Table IV. The metals which are listed in Section 6, Table IV will be determined.
51	Deaerator Vent Gases	Particulates	Particulates will be determined.

Table 18 (Cont'd)

Summary of Effluent Streams to be Analyzed for Lurgi Plant

COAL GASIFICATION

LURGI PROCESS MODEL

Stream No.	Stream Name	Analysis for	Analytical Section Reference
52	Boiler Stacks and Heaters (multiple stacks are involved, including heaters in shift conversion and gas compression areas, see Table 20).	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gases will be analyzed for SO_2/SO_3, NO_x, CO, CO_2, COS, H_2S and CH_3SH and for particulates. Refer to Section 9.
53	Raw Water to Process	Complete Water Analysis	Raw water will be analyzed for all components listed in Section 6, Table IV.
56	Degasser Vent Gases	Trace Sulfur Compounds Hydrocarbons	Vent gases will be analyzed for Thiophene, CS_2, SO_2/SO_3, COS, H_2S and CH_3SH and for benzene, toluene, and other volatile organics. See Section 9.
65	Evaporation and Drift from Cooling Towers	Atmosphere in vicinity of cooling towers to be sampled for: Trace Sulfur Compounds Trace Elements Hydrocarbons and PNA	A high volume sample will be collected and the particulates will be analyzed for the metals listed in Section 7, Table VI. In addition the atmosphere will be sampled for benzene, toluene, and other volatile organics; polynuclear aromatics; and for thiophene, CS_2, SO_2/SO_3, COS, H_2S, and CH_3SH (Section 9).
67	Wet Ash to Mine	Complete coal solids analysis and complete water analysis.	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV.

Table 16 (Cont'd)

Summary of Effluent Streams to be Analyzed for Lurgi Plant

COAL GASIFICATION

LURGI PROCESS MODEL

Stream No.	Stream Name	Analysis For	Analytical Section Reference
68	Ash Water Effluent to Evaporation Ponds*	As for Stream 67	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV.
69	Wet Fine Ash Slurry to Evaporation Ponds*	As for Stream 67	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV.

* Atmosphere over all evaporation and holding ponds and vicinity of all storage tankage to be sampled and analyzed for hydrocarbons and trace sulfur compounds.

Table 19

Coal Input to Lurgi Coal Gasification (2)

Constituent	To Gas Production (Lbs/Hr)	To Fuel Gas Production (Lbs/Hr)
Carbon + HC	1,237,000	265,200
Sulfur	13,400	2,900
Ash	373,200	80,000
Moisture	315,000	67,500
	1,938,600	415,600
MMBTU/HR (H.H.V.)	16,795	3,601

Table 20

Flue-Gas Streams from Boiler and Heater Stacks (2)

El Paso Complex

Component	Lbs/Hr		
	Gas Turbines and Boilers	Steam Superheater	Heaters
Water Vapor	234,600	29,100	6,400
Nitrogen	4,798,700	243,300	53,300
Oxygen	1,006,400	11,800	2,600
Carbon Dixide	552,100	76,500	16,800
Sulfur Dioxide	290	40	10
Nitrogen Oxides (NO_2)	480	70	15
Particulates	NIL	NIL	NIL
	6,592,600	360,800	79,100

3.19 Unit Material Balances

As indicated in Section 1, the object of a material balance around a coal gasification plant, from an environmental viewpoint, is to determine all effluents to the environment and to furnish accountability for all potential pollutants entering the plant or produced in the plant. The analytical summary in Section 3.18 represents the simplest approach to this balance. However, as indicated in Section 1, either a balance may not be made or questions may arise as to the accuracy of some measurements. In this case, analyses may have to be made around certain key units. This would increase the cost considerably. If a balance could not be established after this effort, then it would be necessary to trace each component of interest through every unit. The cost would then be extremely high.

In paragraphs 3.19.1 through 3.19.7 that follow, additional streams from key units are designated as those that may have to be analyzed to complete a balance or find a source of error. The analyses of the streams indicated in these paragraphs require 28 to 29 more samples than the 20 indicated in Table 18. If satisfactory results were not obtained, then it may be necessary to analyze all 72 streams of figure 1.

3.19.1 Coal Preparation

It would be appropriate to determine the concentration of organic and inorganic materials in the run-off from the coal area (streams 2 and 3) as a function of the quantity of rainfall.

3.19.2 Gas Cooling

Streams 15, 21, into gas cooling and streams 12, 23 and 25 from gas cooling would have to be analyzed to check the analysis of stream 24.

3.19.3 Gas Purification

Streams 23 and 26 into gas purification and streams 27, 28 and 29 from the purification must be analyzed to check stream 30.

3.19.4 Sulfur Recovery

In order to check streams 37, 38 and 39 it will be necessary to analyze streams 27, 35 and 36 into the Low-Pressure Stretford Unit and stream 40 out of the unit.

3.19.5 Fuel Gas Treating

It would be wise to analyze stream 72 (solution purge) from the high pressure Stretford unit. How this is done is difficult to predict as this purge may be continuous, intermittent or, in some cases, none at all.

3.19.6 Cooling Water System

This is one of the most critical units for over-all material balance. Good sampling of evaporation and drift losses are difficult and other factors may make the cooling towers research projects in themselves. To get a material balance, it may be necessary to analyze streams 62, 59, 60, 61, and 62 into the system and streams 63, 64 and 65 out of the system. Even this may not be sufficient as trace pollutants can be trapped in slime in the towers. This also may have to be analyzed and its quantity estimated. Whether or not these analyses will check the analysis of stream 65 is uncertain due to the sampling problems mentioned above.

3.19.7 Ash Disposal

The streams into ash disposal should probably be analyzed and compared with effluent streams 67, 68 and 69 to be sure no air pollutants are escaping. This would entail analyses of streams 18, 39, 47, 57, 58 and 66.

3.19.8 Special Unit Material Balance

In some cases, as indicated in Section 1, it may be desirable to determine a material balance around a particular unit. This could arise, for example, when it is necessary to know the contribution of a particular unit to the total effluent/heat load of a plant. Sampling would then be carried out on all the streams in and out of the unit and the samples would be analyzed according to the methods outlined later in Sections 7 through 12. An example of this might be Gas Purification (Section 3.7). All streams in figure 7, together with any others in the particular unit under consideration (e.g., vents, liquid purges, solution makeup, etc.), would then be sampled and analyzed. These analyses, along with heat, steam, hot water, electrical and cooling water requirements, would allow the pollutant/heat load of this unit to be compared with similar units in other plants. It is anticipated that no special revisions of this analytical test plan will be necessary to accommodate such requirements.

4. COAL LIQUEFACTION

Liquefaction, as a term applied to coal processing, is not so definitive as in gasification. The term has been applied generally to processes which produce liquid products from coal, but is also used in connection with solvent or chemical refining processes which desulfurize or de-ash coal (14, 35) and to processes such as combined gasification and catalytic recombination, as in the Fischer-Tropsch synthesis, to produce organic liquids (36). The primary de-ashed product from current solvent-refined coal processes, for example, is not liquid at ambient temperatures (37). And the major products from some "liquefaction" processes are not liquids, but rather solid chars containing most of the ash in the original feed coal.

The COED process chosen for the coal liquefaction model falls into this category. Some 50-60 weight percent of the starting coal feed issues as product char, containing about the same amount of sulfur and having about the same heating value as the feed coal. Economic considerations would probably require that a commercial COED facility include a char gasification facility, and the FMC Corporation, the process developer, is currently engaged in char gasification studies (38).

4.1 System Basis

The COED process has been under development by FMC Corporation as Project COED (Char-Oil-Energy Development) since 1962 under the sponsorship of the Office of Coal Research of the U.S. Department of the Interior (6-16). Bench-scale experiments led the way to design and construction in 1965 of a process development unit (PDU) employing multistage, fluidized-bed pyrolysis to process 50-100 pounds of coal per hour (6). Work with the PDU was extended to other coals in 1966, and hydrotreating of COED oil from the PDU was studied by Atlantic Richfield Company (7). Correlated studies included an investigation of char-oil and char-water slurry pipelining economics, high-temperature hydrogenation for char desulfurization, and an economic appraisal of the value of synthetic crude oil produced from COED oil.

A COED pilot plant able to process 36 TPD of coal and able to hydrotreat 30 BPD of oil was designed and constructed at Princeton, New Jersey in 1970 (10). The pilot plant was operated successfully on a number of coals in 1971-72 (11). Development of the process is continuing, with major funding provided by OCR.

The process basis for our process model is the design study developed by FMC Corporation in 1973 for a "25,000 TPD COED plant" (39). Process flowsheets were developed for the pyrolysis plant, raw oil filtration section, and for the hydrotreating facility. This design feeds 25,512 TPD of an Illinois No. 6-seam coal containing 5.9% moisture, 10.6% ash, and 3.8% sulfur. 12,512 TPD of product char is recovered, along with 3945 TPD of hydrotreated oil (24,925 bpd of indicated 25 API gravity). Flowsheets were not developed for coal preparation, gas treatment, hydrogen manufacture, oxygen manufacture, sulfur production, water and waste treatment, or utilities generation. We have estimated some of the auxiliary requirements (16).

4.2 Process Basis

Figure 18 is a schematic representation of the overall processing scheme. The COED process is a continuous, staged, fluidized-bed coal pyrolysis operating at low pressure and is designed to recover liquid, gaseous, and solid fuel components from the pyrolysis train. Heat for the pyrolysis is generated by the reaction of oxygen with a portion of the char in the last pyrolysis stage and is carried countercurrently through the train by the circulation of hot gases and char. Heat is also introduced by the air combustion of the gas used to dry feed coal and to heat fluidizing gas for the first stage. The number of stages in the pyrolysis and the operating temperatures in each may be varied to accomodate feed coals with widely ranging caking or agglomerating tendencies.

Oil that is condensed from the released volatiles is filtered on a rotary precoat pressure filter and catalytically hydrotreated at high pressure to produce a synthetic crude oil. Medium-Btu gas produced after the removal of acid gases is suitable as clean fuel, or may be converted to hydrogen or to high-Btu gas in auxiliary facilities. Residual char (50-60% of feed coal) that is produced has heating value and sulfur content about the same as feed coal.

A large sample of Illinois coals has been analyzed by Ruch and coworkers (41). As an approximate number, Table 21 lists the mean analytical values of trace elements found for Illinois coals, which represent feed for this study.

This system will produce about 500 TPD of sulfur, in addition to char and syncrude.

The streams indicated for analysis around the COED Process model are summarized in Table 35.

The qualifications and considerations outlined in Section 3.18 for coal gasification are also applicable here. It is intended that all heater and boiler stack effluents shall be analyzed. Similarly, this plant will generate residuals, including hydrotreating and reforming catalysts, sulfated lime sludges from flue-gas treating, and chemical sludges and blowdowns from water treating, gas purification, and tail-gas treating that will probably require special treatment before disposition by the time a facility of this type is constructed. Currently, such materials are commonly trucked to landfill or allowed to accumulate in evaporation ponds.

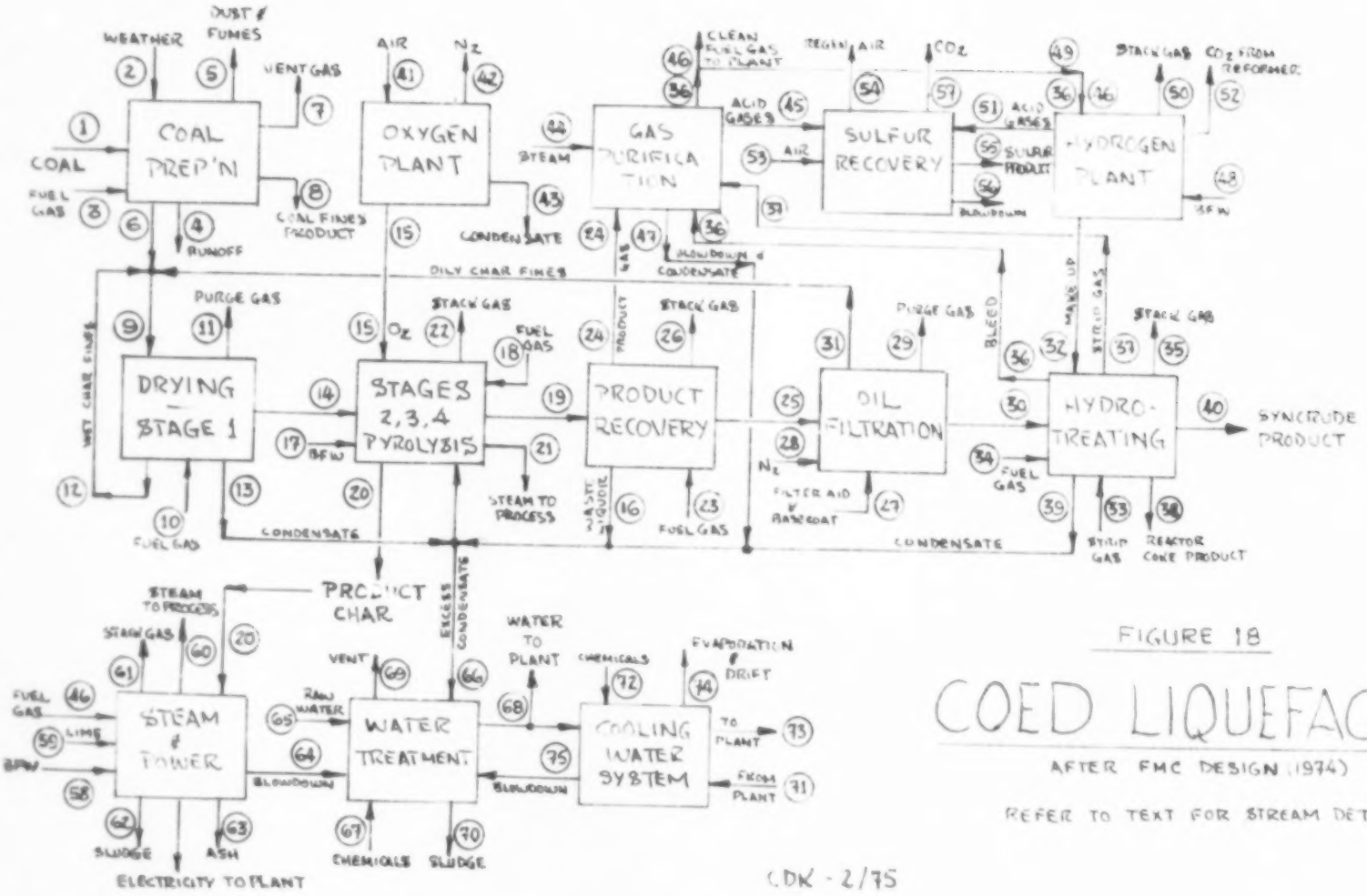


FIGURE 18

COED LIQUEFACTION

AFTER FMC DESIGN (1974)

REFER TO TEXT FOR STREAM DETAILS

CDK - 2/75

Table 21

Mean Analytical Values for 82 Coals from the Illinois Basin (4)

Constituent	Mean		STD	Min	Max
As	14.91	ppm	18.84	1.70	93.00
B	115.74	ppm	51.72	14.00	220.00
Be	1.72	ppm	0.83	0.50	4.00
Br	15.27	ppm	5.60	6.00	32.00
Cd	2.84	ppm	0.32	0.10	65.00
Ce	9.15	ppm	5.76	2.00	34.00
Cl	14.10	ppm	7.48	4.00	54.00
Co	14.09	ppm	6.78	5.00	44.00
Cr	54.30	ppm	19.79	10.00	163.00
Cs	3.04	ppm	1.03	1.00	7.50
Ge	7.51	ppm	7.06	1.00	43.00
Hg	0.21	ppm	0.22	0.03	1.60
Mn	55.16	ppm	40.98	6.00	181.00
Mo	7.96	ppm	5.68	1.00	29.00
Ni	22.35	ppm	10.81	8.00	60.00
P	62.77	ppm	65.56	5.00	339.00
Pb	34.63	ppm	45.94	4.00	218.00
Sb	1.35	ppm	1.42	0.20	8.90
Se	1.99	ppm	0.93	0.69	7.70
Sn	4.56	ppm	8.64	1.00	51.00
V	33.13	ppm	11.65	16.00	78.00
Zn	313.04	ppm	749.92	10.00	5550.00
Zr	72.10	ppm	58.01	12.00	333.00
Al	1.22	%	0.37	0.63	3.04
Ca	0.74	%	0.69	0.05	2.67
Cl	0.15	%	0.19	0.01	0.56
Fe	2.06	%	0.71	0.48	4.32
K	0.14	%	0.04	0.04	0.30
Mg	0.05	%	0.02	0.01	0.17
Na	0.09	%	0.04	0.03	0.19
Si	2.59	%	0.62	0.98	4.63
Ti	0.06	%	0.02	0.02	0.19
SHS	1.54	%	0.62	0.37	3.09
PYS	1.89	%	0.71	0.29	3.79
SUS	0.09	%	0.10	0.01	1.05
TOS	3.51	%	1.12	0.85	5.59
SXRF	3.19	%	1.08	0.79	5.40
ADL	7.70	%	3.47	1.40	16.70
MOIS	10.02	%	4.23	1.90	19.20
VOL	39.80	%	3.17	31.90	46.40
FIXC	48.98	%	3.72	41.30	61.00
ASH	11.28	%	1.98	6.60	15.00
BTU/LB	12748.91		486.50	11982.00	14182.00
C	70.59	%	3.11	62.47	78.94
H	4.98	%	0.24	4.19	5.76
N	1.35	%	0.20	0.93	1.86
O	8.19	%	1.94	4.11	14.16
HTA	11.13	%	2.17	3.79	15.03
LTA	15.22	%	3.22	3.97	23.53

Note: Abbreviations other than standard chemical symbols: organic sulfur (ORS), pyritic sulfur (PYS), sulfate sulfur (SUS), total sulfur (TOS), sulfur by X-ray fluorescence (SXRF), air-dry loss (ADL), moisture (MOIS), volatile matter (VOL), fixed carbon (FIXC), high-temperature ash (HTA), low-temperature ash (LTA).

4.3 Coal Preparation (Figure 19 and Table 22)

Onsite coal storage will be required to provide backup for continuous operations. For 30 days storage, there might be eight piles, each about 200 feet wide, 20 feet high, and 1000 feet long. Containment of airborne dusts is generally the only air pollution control required for transport and storage operations, although odor may be a problem in some instances. Covered or enclosed conveyances with dust removal equipment may be necessary, but precautions must be taken against fire or explosion. Circulating gas streams which may be used to inert or blanket a particular operation or which may issue from drying operations will generally require treatment to limit particulate content before discharge to the atmosphere. Careful management and planning will minimize dusting, wind loss, and the hazard of combustion in storage facilities.

The as-received feed coal employed in this design is indicated to have 10-14 weight percent moisture content. The CMC process basis feeds coal of about 5.9 weight percent moisture to the coal dryer ahead of the first pyrolyzer. Hence the free or surface moisture is assumed to be removed in the upstream coal preparation plant.

Free moisture would be removed from feed coal by milling in a stream of hot combustion gases. The mechanical size reduction of an Illinois coal is expected to generate a considerable quantity of minus 200 mesh fines, especially if appreciable drying accompanies the milling operation. The quantity of such fines has been estimated to be 2 to 8 percent of the feed, depending on the type of equipment that may be used. The ultimate consideration is that the total fines fed to the dryer or to the first pyrolyzer shall not overload the cyclone systems that are provided to effect their separation from the respective effluent streams. Therefore fines generated in coal preparation, amounting to 5 percent of feed coal, will not be charged to pyrolysis but will issue as a fuel product. Coal fines would probably be charged to the char gasification system, if this facility is included.

Clean product gas is fired in the mill heater. About 110 tph of water must be removed if coal is received with 14 percent moisture. This may require the firing of 15-20 tph of product gas with 180-200 tph of combustion air in the milling circuit. Assuming a dry particulate separation system is adequate, bag filters might be used to recover fines from the vented gas following primary classification in cyclones.

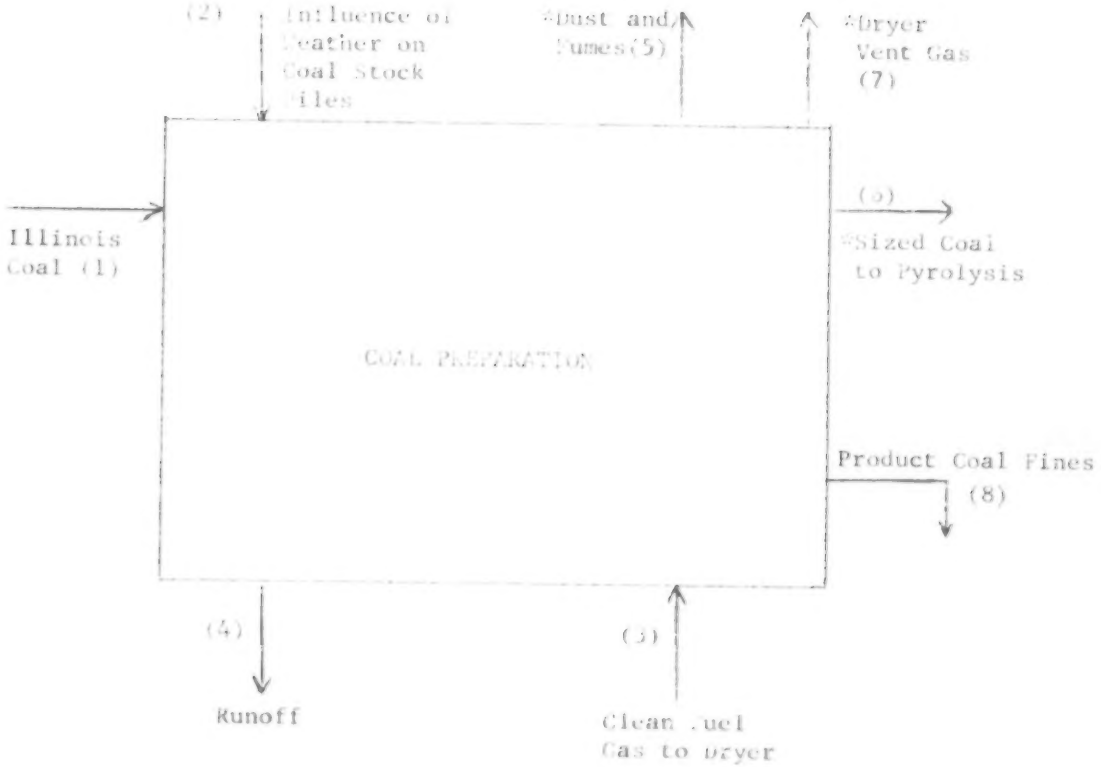


Figure 19

Coal Preparation for COED Plant

Table 22

Coal Preparation for COED Plant

Inlet Streams:

(1) Coal, Illinois No. 6 Seam, 14% moisture; 1237 tph.

(2) Influence of weather on coal stockpiles and open coal operations.

(3) Clean fuel gas to dryer; 455 MM Btu/Hr.

Outlet Streams:

(4) Precipitation runoff to holding ponds. May include wet scrubber aqueous effluents.

*(5) Dust and Fumes. Atmosphere in enclosed working areas to be analyzed per Table 35 for particulates. Discrete stack emissions to atmosphere from enclosed spaces from dust collection equipment to be analyzed per Table 35 for particulates. Atmosphere in vicinity of coal stockpiles, open conveying and handling equipment, and coal fines product collection system to be analyzed per Table 35 for particulates.

*(6) Sized Coal to Pyrolysis, 5.9% moisture; 1063 tph. To be analyzed as feed coal per Table 35.

*(7) Vent gas from dryer containing 108 tph water. Gas stream may require treatment to limit CO content. To be analyzed per Table 35 for particulates, trace sulfur compounds, and CO content.

(8) Product coal fines, 4% moisture; 66 tph.

* Analytical Sample

4.4 Drying and Stage 1 Pyrolysis (Figure 20 and Table 23)

Clean fuel gas is burned substoichiometrically both to dry feed coal and to heat fluidizing gas for the first stage of pyrolysis. Both gas and air feeds to the heaters must be raised in pressure to match the operating pressures of the coal dryer and first stage, nominally 7-8 psig.

Coal is fed from storage hoppers by mechanical feeders into a mixing tee from which it is blown into the dryer with heated transport (recirculated) gas.

A cascade of two internal gas cyclones is provided both the coal dryer and the first pyrolysis reactor. Gas which issues from the first pyrolyzer is circulated through the fluidizing-gas heater for the coal dryer. Gas which issues from the coal dryer passes through an external cyclone and is then scrubbed in venturi scrubber-coolers, which serve to complete the removal of coal and char fines, as well as traces of coal liquids from the gas stream. Fines which are recovered in the external cyclone are passed through a mechanical feeder to a mixing tee where they are injected into the first-stage pyrolyzer by recirculated gas. Water equivalent to that introduced with coal and formed in the combustion processes is condensed from the gas in the scrubbing process.

Scrubber effluent passes into a gas-liquid separator, and the liquor stream is decanted and filtered to remove solids. The solids removed by filtration are indicated to amount to about 1 percent of the coal feed, and the wet filter cake is indicated to be recycled back to coal feed. The decanted liquor, except for a purge stream which, along with the filtrate from the fines filter, balances the removal of water from the section, is pumped back to the venturi scrubbers through water-cooled heat exchangers.

The gas stream which issues from the separator, except for a purge stream which removes the nitrogen introduced in the combustion processes, is compressed and recirculated to the gas heaters. This purge gas stream is essentially the only gaseous release from this section. Like the gas stream envisioned for the coal preparation section (see above), it is indicated to contain about 3.7 percent carbon monoxide, and will probably require further treatment before it may be released to the atmosphere. It may be possible to inject it into a boiler stack(s) along with air or oxygen to reduce CO emission. Alternatively the stream(s) may have to be incinerated in specific equipment for this purpose with additional fuel. The gas stream in this case is indicated to be sulfur-free.

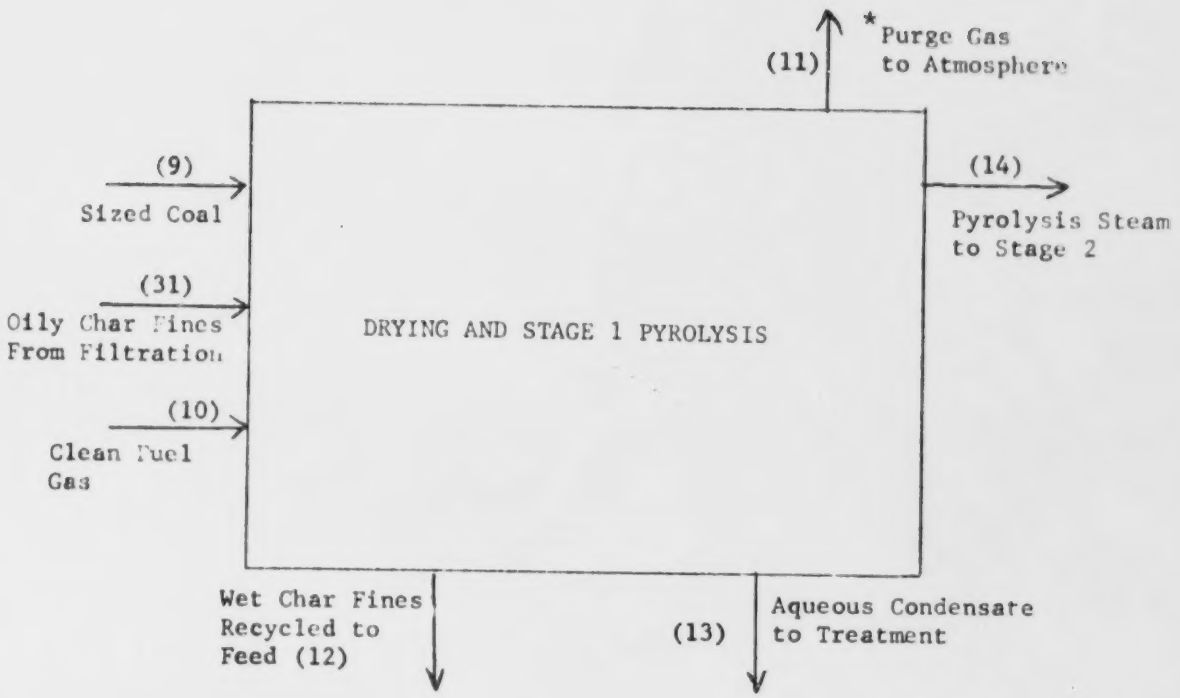


Figure 20

Drying and Stage 1 Pyrolysis

Table 23

Drying and Stage 1 Pyrolysis

Inlet Streams:

(9) Sized Coal; 1063 tph; plus Recycle Wet Char Fines; 22 tph.

(10) Clean Fuel Gas; 25 tph.

(31) Oily Char Fines from Filtration; 15.2 tph.

Outlet Streams:

*(11) Purge gas to atmosphere; 366 tph. May require treatment to limit CO content. To be analyzed for particulates, trace sulfur compounds, and CO content per Table 35.

(12) Wet, oily char fines separated at fines filter; 22 tph. Recycled to coal feed.

(13) Aqueous condensate; 93.5 tph. 83.3 tph directed to last pyrolyzer. 10.2 tph directed to water treatment.

(14) Pyrolysis Stream to Stage 2; 978 tph.

* Analytical Sample.

4.5 Stages 2,3,4 Pyrolysis (Figure 21 and Table 24)

Coal which has undergone first-stage pyrolysis (at temperatures of about 550-600°F) is passed out of the stage into a mixing tee, from which it is transported into the second stage by heated recycle gas. Pyrolysis stages 2,3, and 4 are cascaded such that pyrolyzed solids pass through the stages in sequence in transport gas streams. Superheated steam and oxygen are injected into the last stage, where heat is released by partial combustion. Substantial recycle of hot (~1550°F) char from this last stage is used to supply heat to stages 2 and 3, in which it otherwise serves as an inert diluent. Similarly, hot gas which issues from the last stage is passed countercurrently through the cascade, serving also as the primary fluidizing medium in these reactors. Stages 2 and 3 operate at about 850° and 1050°F respectively.

The pyrolyzer vessels are each about 60-70 feet in diameter. A total of eight pyrolyzers in two trains is required to process the indicated feed coal. All fluidized vessels are equipped with internal dual-cascade cyclone systems.

Gas which issues from the second pyrolyzer passes through an external cyclone before being directed to the product recovery system. Fines which are separated are directed, along with product char from the last stage, to a fluidized bed cooler, which is used to generate 265,000 lb/hr of 600 psia steam. First-stage recycle gas is used to fluidize the char cooler, and the gas which issues from the cooler is directed back to the venturi scrubbers in the first section after it has passed through an external cyclone. Fines from this cyclone are added to the char make from the last stage. Product char is available at this point at 800 F. About 180,000 lb/hr of 150 psia steam may additionally be generated from the char if suitable equipment can be designed to abstract its sensible heat.

Because the system is otherwise closed, the only possible major atmospheric effluents from this section are the products of combustion from the heaters used to superheat the steam and oxygen feeds to the last pyrolysis stage. We have assumed clean product gas for this service also. About 10.5 tons of gas is required, along with about 105 tons of air per hour. The combustion products should be dischargeable directly in this case without further treatment.

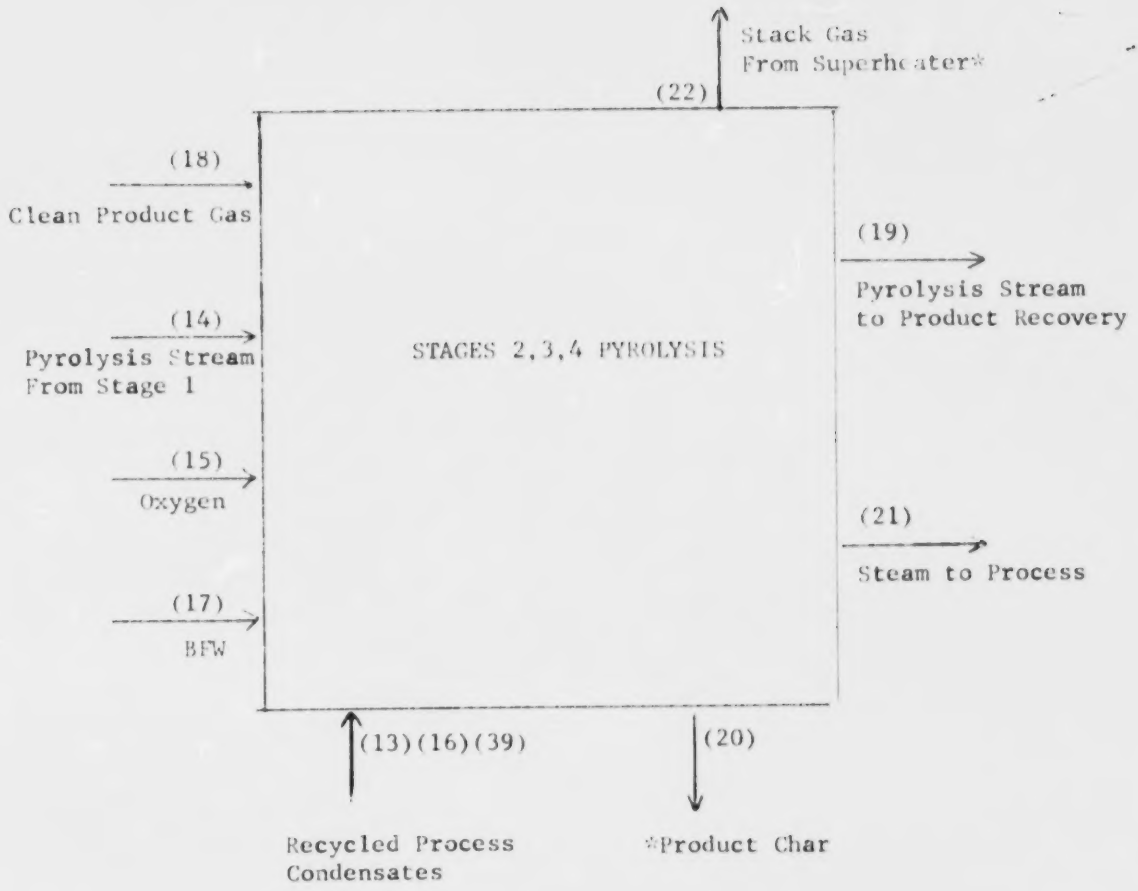


Figure 21

Stages 2,3,4 Pyrolysis

Table 24

Stages 2,3,4 Pyrolysis

Inlet Streams:

(14) Pyrolysis Stream from Stage 1; 978 tph.

(15) Oxygen from Oxygen Plant; 156.5 tph.

(39)(13)(16) Recycled process liquors as steam to last pyrolyzer; 337 tph.

(17) BFW to fluidized bed char cooler and aftercooler; 900 gpm.

(18) Clean Product Gas to Superheaters; 10.5 tph.

Outlet Streams:

(19) Pyrolysis Stream to Product Recovery; 1088 tph.

*(20) Product char; 521 tph. To be analyzed for trace sulfur and trace elements per Table 35.

(21) 600 psia steam; 265,000 lb/hr and 150 psia steam; 180,000 lb/hr from char cooling to process.

*(22) Stack gas from superheaters; 115 tph. To be analyzed per Table 35 for particulates and trace sulfur compounds.

* Analytical Sample.

4.6 Product Recovery (Figure 22 and Table 25)

Gas from the pyrolysis section is cooled and washed in two cascaded venturi scrubber stages to condense oil and solid components from the gas stream. The gas which issues from the second scrubber gas-liquid separator is passed through an electrostatic precipitator to remove microscopic droplets, and is then cooled to 110°F by cold-water exchange to condense water. About a quarter of the gas stream is compressed and reheated for use as transport gas in the pyrolysis train. The remainder issues from the system as raw product gas, which is to be directed to an acid-gas removal system.

The oil and water condensed from the gas stream in the scrubber-coolers is decanted and separates into three phases: a light oil phase, a middle (aqueous phase), and a heavy oil phase. The oil phases are collected separately for dehydration in steam-jacketed vessels. The combined dehydrated oil is pumped to the COED oil filtration system.

A recycle liquor pump takes suction from the middle phase in the decanter. Recycle liquor is cooled in cold-water exchangers before being injected into the venturi scrubbers. Water condensed from the incoming gas leaves the section as a purge ahead of the recycle liquor coolers, and is indicated to be recirculated to the last pyrolysis stage.

The only major effluents to the atmosphere from this section are the combustion gases from the recycle transport-gas heater. Since clean product gas is fired in this heater, the combustion gases should be dischargeable directly.

Vents from the oil decanters and dehydrators are indicated to be directed to an incinerator. Under normal operation, and with adequate condensing capacity in the vapor takeoffs from the dehydrators, vent flow should be minimal.

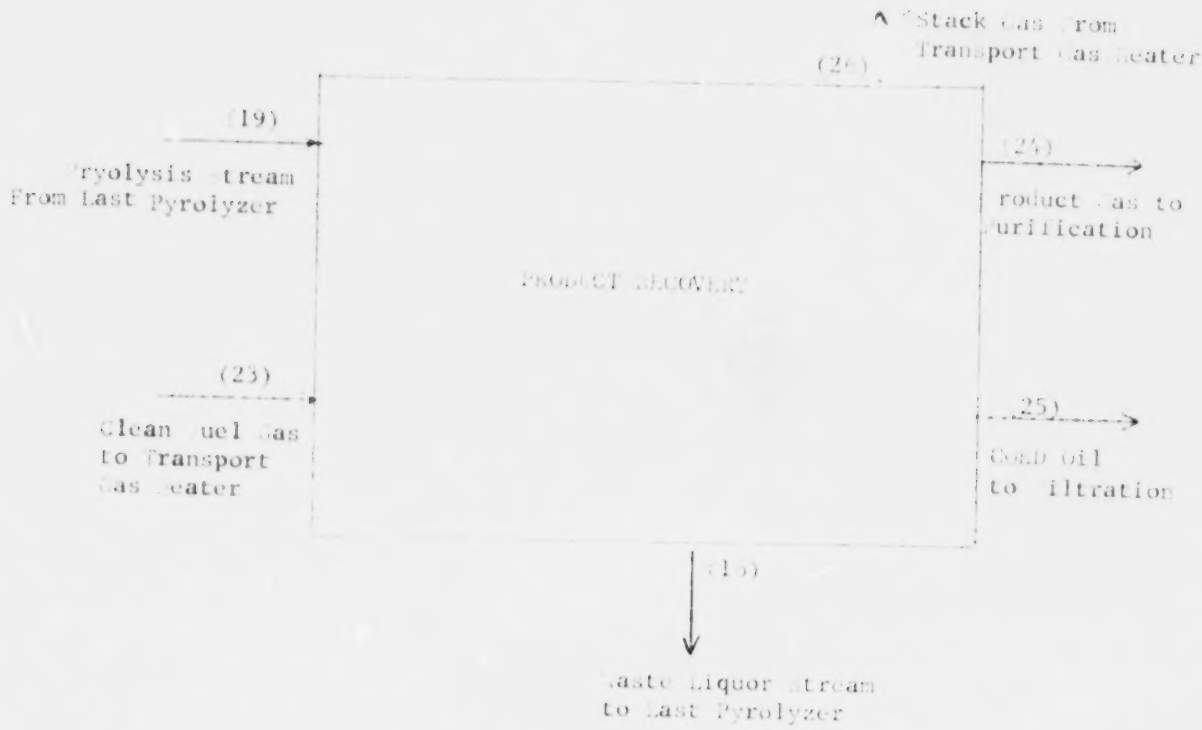


Figure 22

Product Recovery

Table 25

Product Recovery

Inlet Streams:

(19) Pyrolysis Stream from Last Pyrolyzer; 1088 tph.

(23) Clean Fuel Gas to Transport Gas Heater; 3.1 tph.

Outlet Streams:

(16) Waste Liquor Stream to Last Pyrolyzer; 237 tph.

(24) Product Gas to Gas Purification; 513 tph.

(25) COED oil to Oil Filtration; 200 tph.

*(26) Stack Gas from Transport Gas Heater; 35 tph, to be analyzed per Table 35 for particulates and trace sulfur compounds.

* Analytical Sample.

4.7 Oil Filtration (Figure 23 and Table 26)

FMC has designed a filtration plant to handle the COED raw oil output based on filtration rates demonstrated in its pilot plant. The system employs ten 700 ft^2 rotary-pressure precoat filters to remove char fines from the raw oil ahead of hydrotreating. Each filter is operated on a 7-hour precoat cycle, followed by a 41-hour filtration cycle.

Both the precoat and the raw oil to filtration are heated, using steam, to about 340 F. Inert gas (nitrogen) is compressed, heated, and recirculated for pressurizing the filters. The gas purge from the system, equivalent to the nitrogen makeup, is directed to a boiler stack. It is indicated to contain only trace quantities of combustibles and sulfur.

Hot filter cake (38% oil, 52% char, 10% filter aid at 350 F) is discharged at the rate of about 15 tph, and is indicated to be added to the plant's char output on a process basis. FMC has recently indicated that filter cake will instead be recycled to coal feed. Filtered oil is directed to the hydrotreating facility.

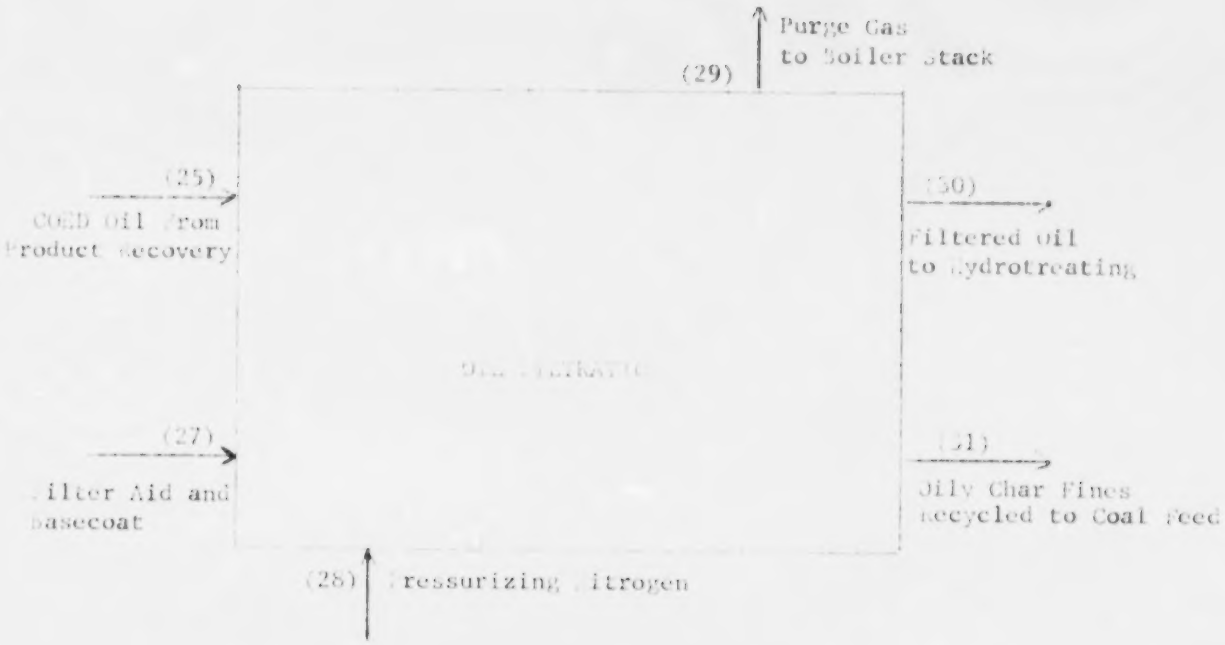


Figure 23

Oil Filtration

Table 2b

Oil Filtration

Inlet Streams:

(25) COED Oil from Product Recovery; 200 tph.

(27) Filter aid and Basecoat during filter precoat cycle; 1.5 tph.

(28) Pressurizing nitrogen from oxygen plant; 0.5 tph.

Outlet Streams:

(29) Purge gas directed to incinerator or boiler stack; 0.5 tph.

(30) Filtered Oil to Hydrotreating; 186 tph.

(31) Oily char fines containing 1.5 tph filter aid; 15.2 tph. Recycled to coal feed.

4.8 Hydrotreating (Figure 24 and Table 27)

Hydrotreating is employed to upgrade the heavy pyrolysis oil through the addition of hydrogen, which serves to convert sulfur to hydrogen sulfide, nitrogen to ammonia, and oxygen to water, as well as to increase the oil's hydrogen content through saturation reactions. Hydrotreating is performed catalytically in the FMC pilot plant at 750 to 800 F and at total pressures of 2000-3000 psig; conditions which also promote some cracking reactions.

In the FMC base design, hydrotreating is indicated to be performed at 750°F and at a total pressure of 1710-1720 psia. Filtered oil from the filtration plant is pumped, along with hydrogen from a reforming plant and some recycled oil, through a gas-fired preheater into initial catalytic guard reactors. The guard reactors are intended to prevent plugging of the main hydrotreating reactors by providing for deposition of coke formed in the system on low surface-to-volume packing.

The hydrotreating reactors are indicated to be three-section, down flow devices. The gas-oil mixture from the guard bed is introduced at the reactor head along with additional recycle hydrogen. Recycled oil and hydrogen at low temperature (100-200°F) are introduced between the catalyst sections in the reactor to absorb some of the exothermic heat of reaction.

The hydrotreated effluent is cooled and flows into a high-pressure flash drum, where oil-water-gas separation is effected. About 60 percent of the gas which separates is recycled by compression to the hydrotreaters. The remainder is indicated to be directed to the hydrogen plant.

A little less than half of the oil which separates is recycled to the hydrotreaters. The remainder, taken as product, is depressured into a receiving tank. From the tank it is pumped into a stripping tower, where clean product gas is used to strip hydrogen sulfide and ammonia.

Clean product gas is used also to strip ammonia and H_2S from the water which separates from hydrotreater effluent. Stripped water is indicated to be recycled to the last pyrolysis stage. The gas effluents from the strippers are indicated to be directed to gas clean up.

The only major effluents to atmosphere from this section are the combustion gases from the hydrotreater preheater. About 4.5 tph of product gas is consumed, along with about 84 tph of combustion air. The products of combustion should be dischargeable directly without further treatment.

The process design basis does not provide for catalyst replacement in this section. Nor are facilities included for presulfiding catalyst, if this be required, or for regenerating catalyst.

We have assumed that regeneration, if it is practiced, will occur off site. Moreover, we have assumed that the hydrotreaters will be designed to run continuously between maintenance shutdowns.

Provisions for depressuring and inerting the hyirotreater preliminary to catalyst removal should not result in emissions to atmosphere, since gaseous effluents may be recycled to the hydrogen plant gas treatment section, or to the main gas-treating section. Ammonium sulfide, which is produced in the hydrotreater and which is stable at reaction conditions, decomposes at low temperatures and pressure to release additional ammonia and H_2S into the inerting medium. Metal carbonyls may also be present, and special precautions may be required if these are found in significant concentration.

Gaseous effluent which results from inerting the system after catalyst replacement may require treatment to remove particulates. In general, the same procedures used to replace catalyst in the hydrotreater may also be applied to changeout of the packing or catalyst in the guard reactors.

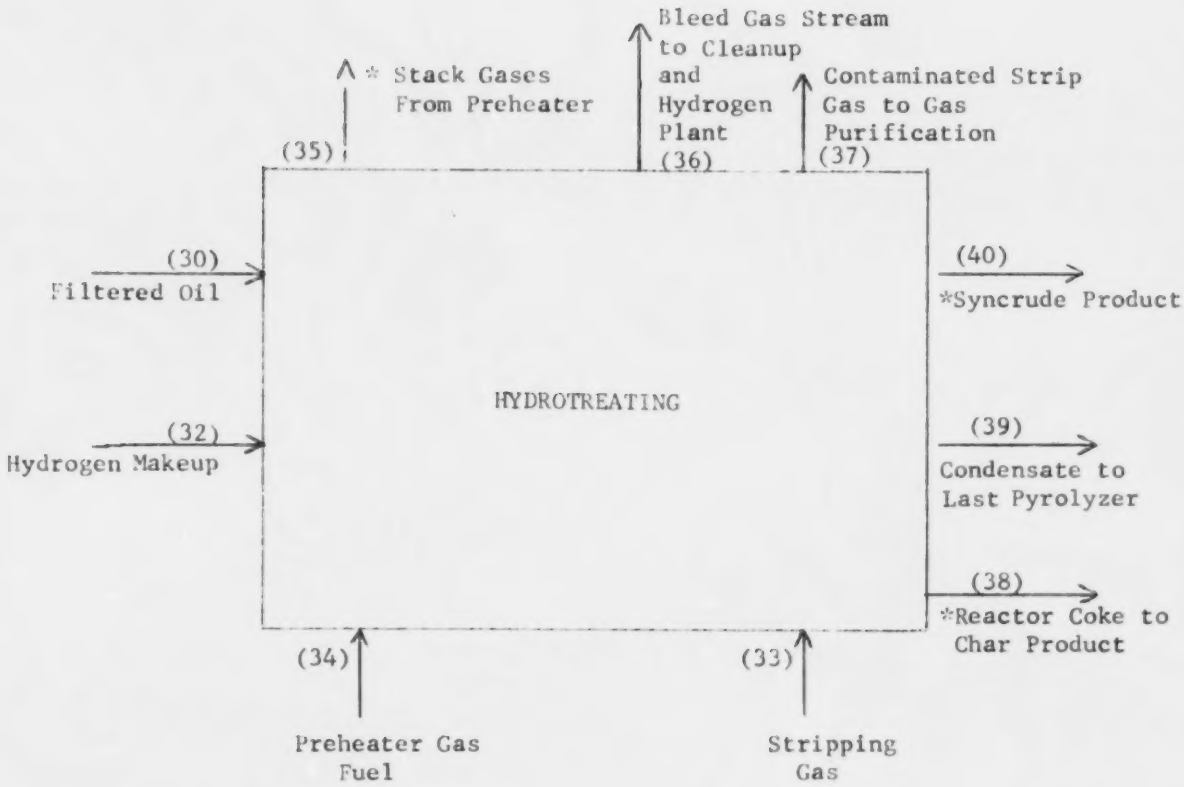


Figure 24

Hydrotreating

Table 27

Hydrotreating

Inlet Streams:

(30) Filtered Oil from Filtration; 186 tph.

(32) Hydrogen Makeup from Hydrogen Plant; 28.4 tph.

(33) Clean Product Gas Stripping Medium; 103 tph.

(34) Clean Product Gas to Preheater; 11.8 tph.

Outlet Streams:

*(35) Stack Gases from Preheater; 130 tph. To be analyzed for particulates and trace sulfur compounds per Table 35.

(36) Bleed Gas Stream to Cleanup and Hydrogen Plant; 29 tph.

(37) Contaminated Stripping Gas to Gas Purification; 107 tph.

*(38) Reactor Coke to Product Char; 0.04 tph. To be analyzed for trace elements for Table 35.

(39) Contaminated Condensate to Last Pyrolyzer; 16.6 tph.

*(40) Syncrude Product; 164.4 tph. To be analyzed for trace sulfur compounds and trace elements per Table 35.

* Analytical Sample.

4.9 Oxygen Plant (Figure 25 and Table 28)

The oxygen plant provides a total of 3760 tons per day of oxygen to the last pyrolysis stage. The only effluents to the air from this facility should be the other components of air, principally nitrogen About 340 MM scfd of nitrogen will be separated. Some of this nitrogen may be used to advantage in the plant to inert vessels or conveyances, to serve as transport medium for combustible powders or dusts, to serve as an inert stripping agent in regeneration or distillation, or to dilute other effluent gas streams. Nitrogen is also indicated to be used to pressurize the rotary pressure raw-oil filters.

About 440 MM scfd of air is taken into the oxygen facility. Placement of the oxygen facility will depend in part on the desire to maintain the quality of the air drawn into the system and, especially, to minimize interference from plant effluents.

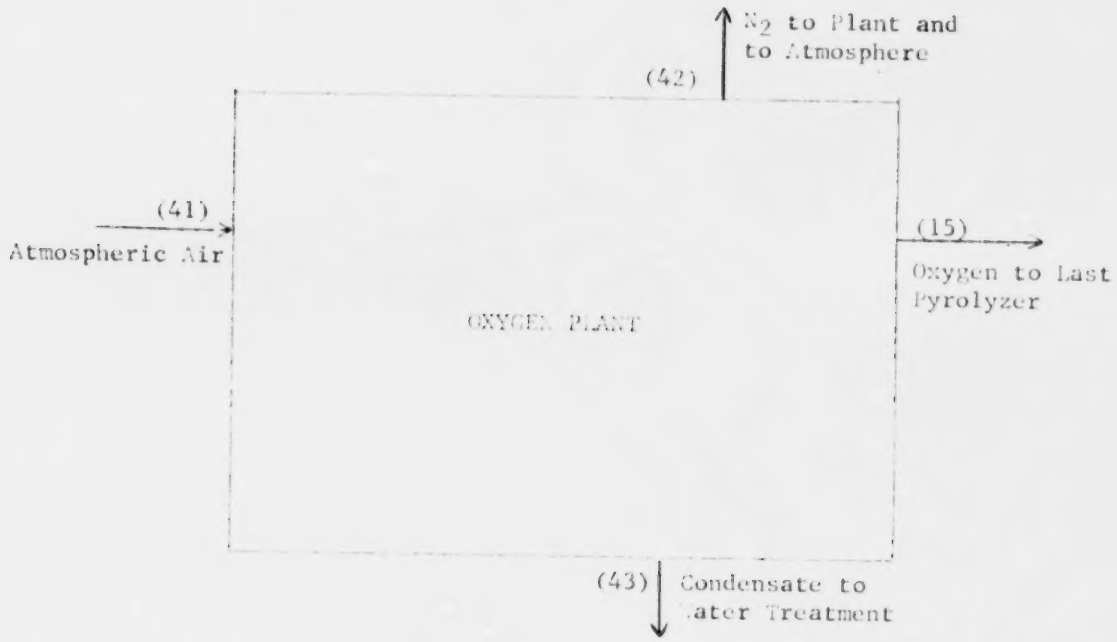


Figure 25

Oxygen Plant

Table 28

Oxygen Plant

Inlet Streams:

(41) Atmospheric air intake; 440 MM SCFD.

Outlet Streams:

(15) Oxygen to Last Pyrolyzer; 156.5 tph.

(42) Nitrogen to Atmosphere and/or Plant; 340 MM SCFD.

(43) Water Condensate to BFW Treatment; 17 gpm.

4.10 Gas Purification (Figure 26 and Table 29)

The acid-gas removal process to be used in this facility has not been specified by FMC. Sulfinol and hot carbonate have been tentatively considered.

The primary feed to this unit would be the product gas stream separated from the product recovery system (513 tph). Contaminated product gas used for stripping the water and oil effluents from hydrotreating (107 tph) may also be returned to this unit; however, since this stream contains ammonia, it may be preferable to treat it separately.

The particular choice of acid gas removal process may depend on the nature and quantity of "trace" contaminants present in the gas to be treated. FMC has not reported on the quantity and nature of the sulfurous contaminants in raw gas. COS has been found in some streams.

In our basis we have assumed that the "Benfield" hot potassium carbonate gas purification system will be used. In the Benfield system, gas absorption takes place in a concentrated aqueous solution of potassium carbonate which is maintained at above the atmospheric boiling point of the solution (225-240 F) in a pressurized absorber. The high solution temperature permits high concentrations of carbonate to exist without incurring precipitation of bicarbonate.

Partial regeneration of the rich carbonate solution is effected by flashing as the solution is depressured into the regenerators. Low-pressure steam is admitted to the regenerator and/or to the reboiler to supply the heat requirement. Regenerated solution is recirculated to the absorbers by solution pumps. Stripped acid gas flows to the sulfur recovery plant after condensation of excess water. Depressurization of the rich solution from the absorber through hydraulic turbines may recover some of the power required to circulate solution.

Raw product gas from the product recovery section must be compressed for effective scrubbing. We have estimated that the compressor driver will require the equivalent of 500,000 lb/hr of high-pressure steam to handle the primary raw gas stream. Some 1,400,000 gph of solution must be circulated, requiring the equivalent of 5700 kW. Some 450 MM Btu/hr is required for regeneration, supplied as steam, and about this same cooling duty will be required. Additionally, some 100,000 lb/hr of high-pressure steam, 1200 kW, and 95 MM Btu/hr as low-pressure steam, as well as the corresponding quantity of cooling water, will be required to treat the stripping gas from hydrotreating.

Clean gas may be directed to the various fired heaters throughout the plant, and to the utility boiler. There should be no discharge to the atmosphere from the acid-gas removal section.

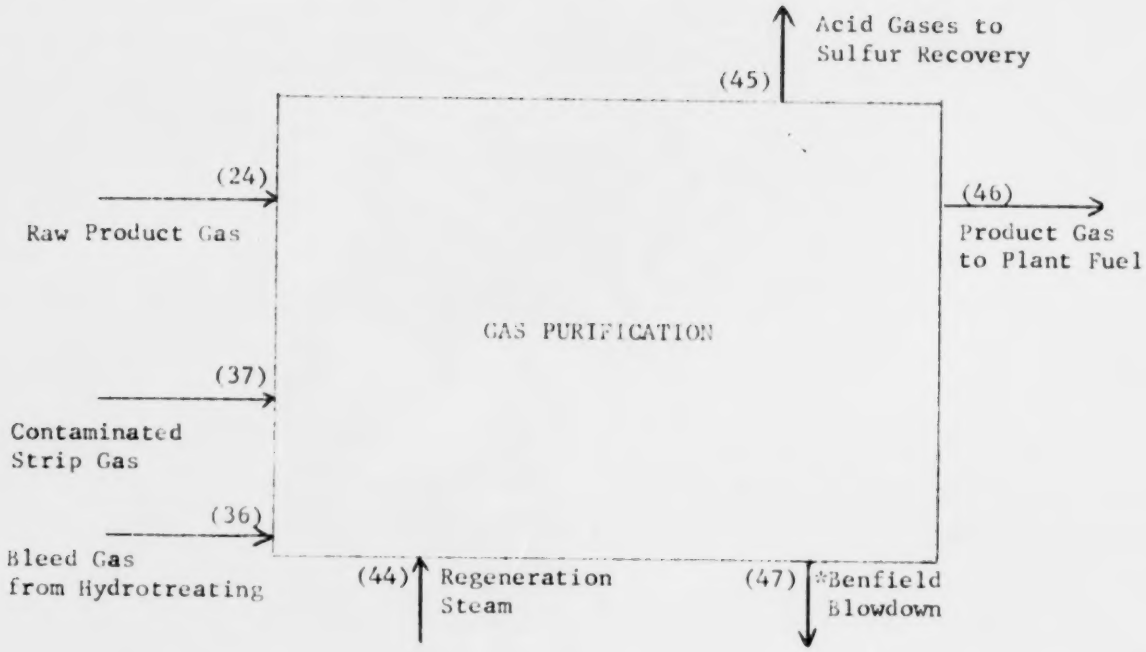


Figure 26

Gas Purification for COED Plant

Table 29

Gas Purification for COED Plant

Inlet Streams:

(24) Product Gas from Product Recovery; 513 tph.

(36) Bleed Gas from Hydrotreating; 29 tph.

(37) Contaminated Stripping Gas from Hydrotreating; 107 tph.

(44) 150 psia Steam to Regenerators; 381,000 lb/hr.

Outlet Streams:

(45) Acid gases to Sulfur Recovery; 315 tph.

(46) Product Gas to Plant Fuel and to Hydrogen Plant; 171 tph dry basis.

*(47) Spent Benfield blowdown requires special treatment. To be analyzed per Table 35 for trace sulfur compounds and trace elements.

* Analytical Sample.

4.11 Hydrogen Plant (Figure 27 and Table 30)

The COED process gas product is indicated to be the source of hydrogen for the hydrotreating of raw COED oil. We have assumed that steam reforming will be used to produce the hydrogen requirement.

COED process gas at 15 psia is compressed to 410 psia and passed through a sulfinol system to remove CO_2 and H_2S. Regenerated acid gases are directed to the sulfur recovery plant. The cleaned process gas containing about 1 ppm H_2S is divided into a fuel gas stream and a process feed gas stream. The process feed gas is passed over a zinc oxide sulfur guard bed to remove sulfur traces, and is then heated by combustion of the fuel gas and hydrogenated with recycle product hydrogen to remove unsaturates. Steam is injected, and reforming and shifting occur catalytically according to:

$$CH_4 + H_2O \longrightarrow CO + 2H_2 \quad \text{(reforming)}$$
$$CO + H_2O \longrightarrow CO_2 + H_2 \quad \text{(CO shift)}$$

CO_2 formed in the reactions is removed in a second scrubber-absorber and the process gas is finally methanated catalytically to convert residual CO to methane according to $3H_2 + CO \longrightarrow CH_4 + H_2O$. Resulting product gas is available at 200 psig.

The bleed gas from the hydrotreating plant, containing about 2 percent H_2S and about 0.1 percent ammonia, is indicated to be returned to the hydrogen plant for reprocessing. It may be preferable to first scrub this stream with water separately to remove the ammonia trace. About 3.5 tph of H_2S must also be removed from this stream, and the H_2S residual, after water scrubbing, would be removed in an acid gas scrubber and directed to the sulfur recovery plant.

The major gaseous effluents from the hydrogen plant will be the products of combustion from the fired heaters and the CO_2 stream removed from the processed gas after reforming. Since clean product gas is consumed in the heaters, the products of combustion should be dischargeable directly. Some 23 tph of gas is fired.

About 60 tph of CO_2 will be removed from the process gas, and this too may be discharged, although there may be incentive to recover some or all of this stream for sale, since its purity should be high.

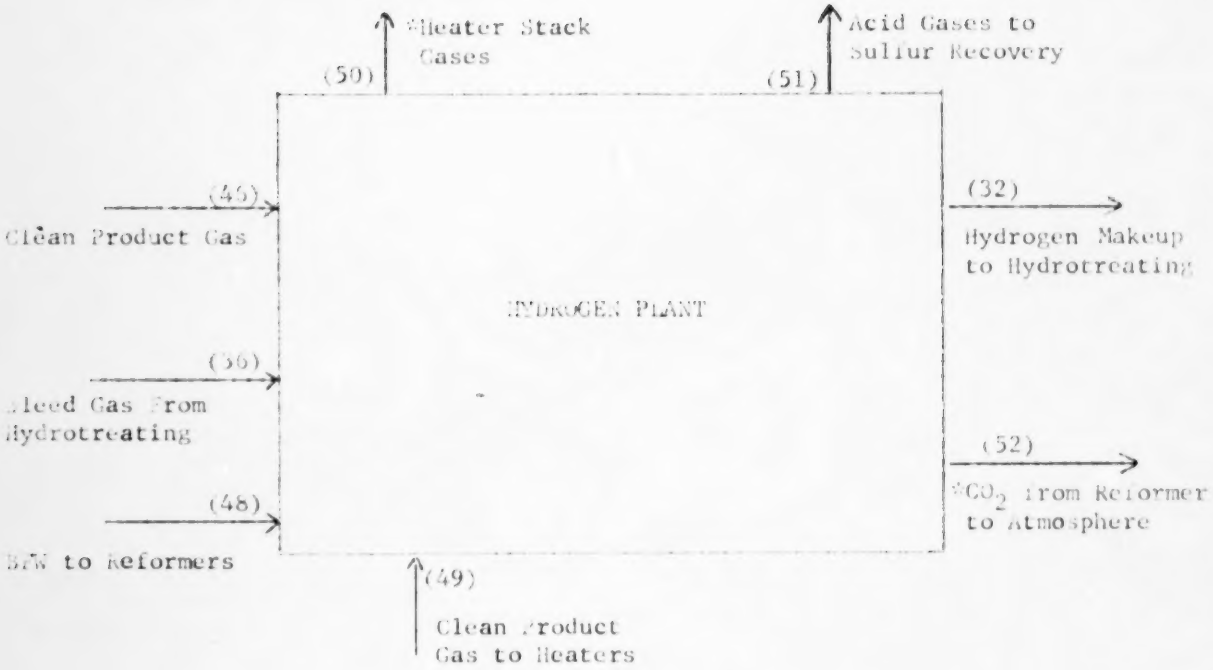


Figure 27

Hydrogen Plant

Table 30

Hydrogen Plant

Inlet Streams:

(36) Bleed Gas from Hydrotreating; 29 tph.

(46) Clean Product Gas to Reformers; 25 tph.

(48) BFW to Reformers; 43 tph net consumption. Excess condensate returned to Water Treatment.

(49) Clean Product Gas to Fired Heaters; 23 tph.

Outlet Streams:

(32) Hydrogen Makeup to Hydrotreating; 28.4 tph.

*(50) Stack Gases from Fired Heaters. To be analyzed for particulates and trace sulfur compounds per Table 35.

(51) Acid Gases to Sulfur Recovery.

*(52) CO_2 from reformers; 60 tph. To be analyzed for trace elements per Table 35.

4.12 Sulfur Recovery (Figure 28 and Table 31)

The type of sulfur plant that will be used has not been specified by FMC. The combined acid-gas streams resulting from treatment of raw product gas (pyrolysis gas) and hydrotreating bleed gas would appear to yield an H_2S concentration of about 7 percent based on gas analyses presented in the FMC design. Additional concentrated H_2S streams may result from treatment of sour water and stripping gas. FMC has indicated that high-sulfur Illinois coals will yield H_2S levels in the range of 10-20 percent.

We have assumed that acid gas will be sufficiently high in H_2S content to permit use of a Claus recovery system. Tail gas from the Claus unit must be desulfurized, however. Several processes have been developed for this purpose. FMC indicates that the Beavon or Shell Claus Off-Gas Treating (SCOT) process may be employed.

The Beavon system catalytically hydrogenates the SO_2 over cobalt-molybdate. The catalyst is also effective for reacting CO, which may be present, with water to form hydrogen and for the reaction of COS and CS_2 with water to form H_2S.

The hydrogenated stream is cooled to condense water, and the H_2S stream is fed into a Stretford unit to recover sulfur in elemental form. Treated tail gas may contain less than 200 ppm sulfur, with almost all of this being carbonyl sulfide. Condensate may be stripped of H_2S and directed to boiler feed water treatment.

About 500 tpd of elemental sulfur will be separated at the sulfur plant, depending on the sulfur content of the feed coal and on the processing employed. Total sulfur emission to the atmosphere may be held to less than 200 lbs/hr, and the treated tail gas may be directed to a boiler stack for disposal. The small air stream used to regenerate the Stretford solution in the tail gas treatment plant may also be so directed.

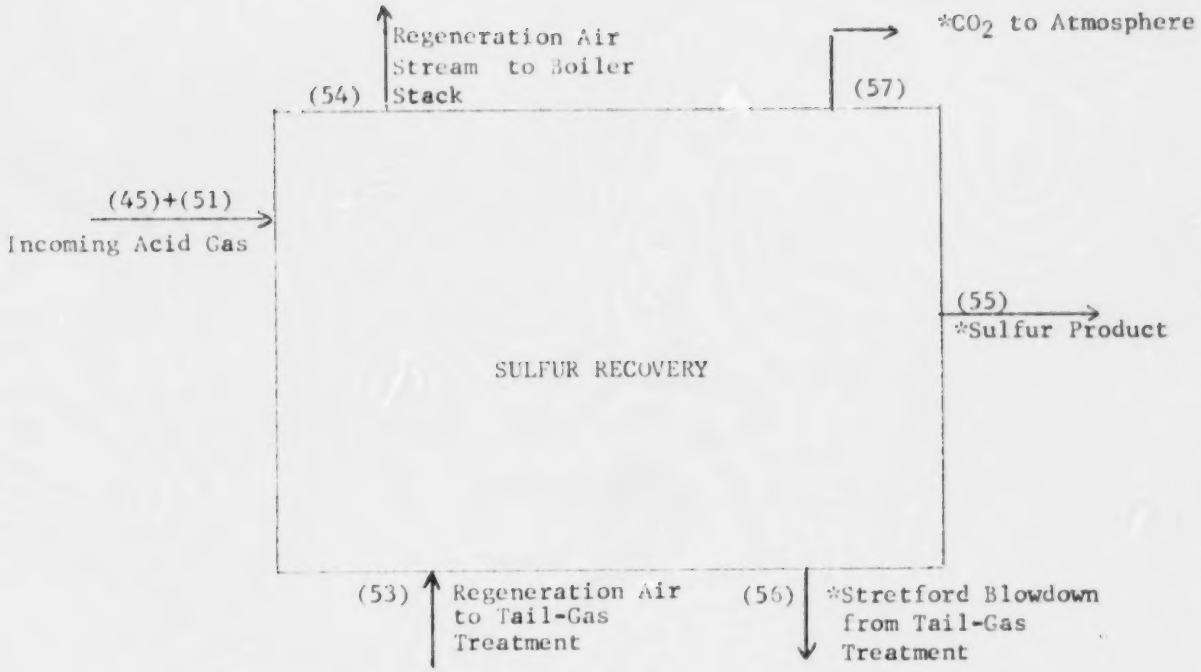


Figure 28

Sulfur Recovery for COED Plant

Table 31

Sulfur Recovery

Inlet Streams:

(45)(51) Incoming Acid Gases (330 tph) containing 23 tph H_2S.

(53) Regeneration Air to Tail-Gas Treatment; 0.7 MM SCFD.

Outlet Streams:

(45) Regeneration Air Stream to Boiler Stack; 0.7 MM SCFD.

*(55) Sulfur Product; 510 tpd. To be analyzed for trace elements per Table 35.

*(56) Stretford blowdown from tail-gas treatment, to be analyzed for trace elements and trace sulfur compounds per Table 35. May require special treatment.

*(57) CO_2 stream to Atmosphere contains less than 200 ppm sulfur. To be analyzed for trace sulfur per Table 35.

* Analytical Sample.

4.13 Power and Steam Generation (Figure 29 and Table 32)

We have in this study considered that dirty fuels would not be combusted in the plant; therefore, clean product gas would be used for the generation of steam and power requirements. However, the total utility balances require some additional fuel source. Of the 513 tph of contaminated product gas issuing from the product recovery system, there is net 171 tph of dry gas available from the acid-gas removal system. Some 25 tph is required as feed to the hydrogen plant, leaving the net available gas for fuel as 146 tph. The gas is estimated to have a higher heating value of 505 Btu per scf, so that the total available fuel gas equivalent is about 4180 MM Btu per hour.

Net steam requirements for the facility total 783,000 lb/hr, equivalent to a 1130 MM Btu/hr fuel requirement. Net electrical power requirements total 93,200 kW, equivalent to 902 MM Btu/hr of additional fuel. The plant otherwise fires fuel equivalent to 2842 MM Btu/hr in process heaters. Hence the total requirement, 4847 MM Btu per hour, cannot be supplied by the product gas stream alone. The shortfall, equivalent to 694 MM Btu/hr, would presumably come from char.

We have considered that the 2032 MM Btu/hr fuel equivalent required at the power plant could be supplied by the combinative firing of product char and product gas in suitably designed boilers. The fuel requirement is such that if all of the char required to supply the fuel shortfall, about 30 tph, is fired in the power plant along with about 47 tph of product gas, the sulfur emission would be such that flue-gas treatment would be required. About 2.1 tph of SO_2 would be emitted, equivalent to about 2.0 lb/MM Btu, which is above the level permitted by current standards for solid fuels.

We have assumed that char will be combusted in the power plant to make up the fuel shortfall and that flue gas will be treated with a limestone process. We recognize that some char treatment process is practically required in a commercial design, so that it is likely that clean fuel gas of low heating value will be available from char in an integrated facility.

We note, however, that only that portion of stack gases derived from char burning needs be treated in our assumed case. Only a small amount of product gas would be fired with char to stabilize the char combustion in order to minimize the volume of stack gas which is treated.

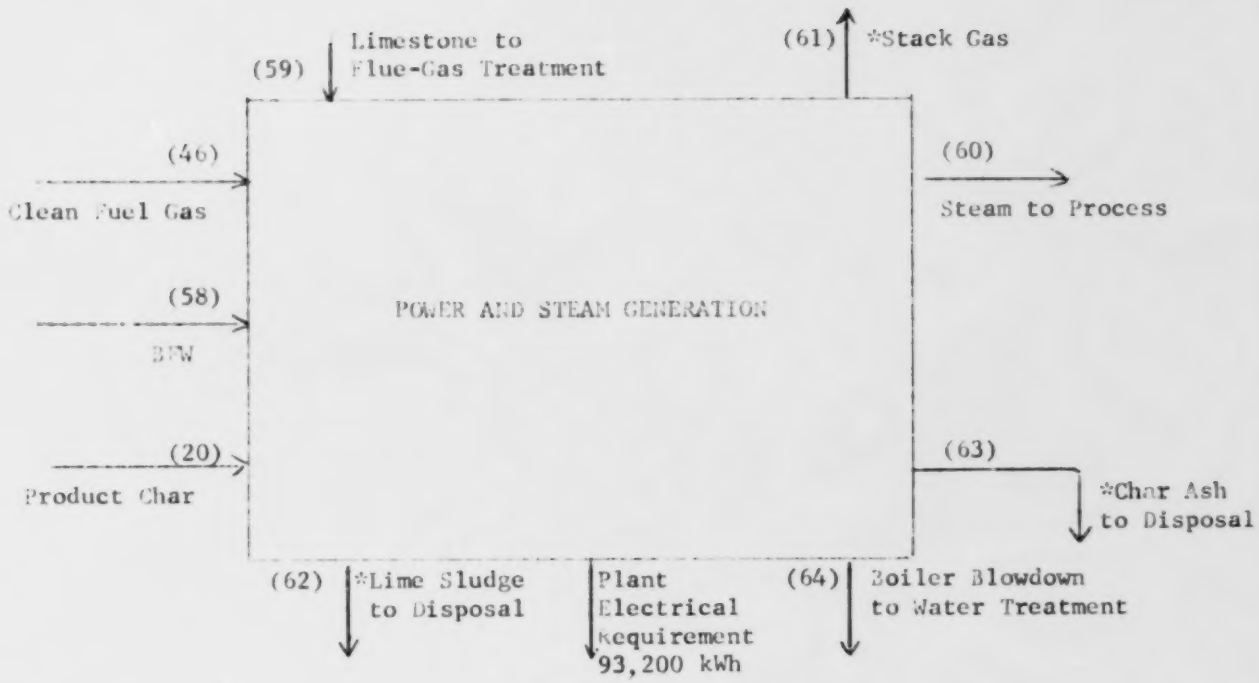


Figure 29

Power and Steam Generation

Table 32

Power and Steam Generation for COED Plant

Inlet Streams:

(20) Product Char; 30 tph.

(46) Clean Fuel Gas; 47 tph.

(58) BFW; 783,000 lb/hr.

(59) Limestone to Flue-Gas Treatment.

Outlet Streams:

(60) Steam to Process; 277,000 lb/hr 150 psia and 506,000 lb/hr 600 psia.

*(61) Stack Gases. Complete stack gas analysis, including particulates and trace sulfur compounds per Table 35.

*(62) Lime Sludge to Disposal. To be analyzed for trace elements and trace sulfur compounds per Table 35. May require special treatment.

*(63) Char Ash to Disposal; 6.4 tph. To be analyzed for trace elements and trace sulfur compounds per Table 35. May require special treatment

(64) Boiler Blowdown to Water Treatment.

* Analytical Sample.

4.14 Water Treatment (Figure 30 and Table 33)

Analyses of the aqueous condensates produced in the pyrolysis and hydrotreating plants have not been specified in the FMC design. FMC has indicated that these streams would be preferentially recycled to the last, or hottest pyrolyzer, or to char gasification if it be included, after minimal processing to strip ammonia and hydrogen sulfide.

Recycle to a high-temperature char gasification system should present no difficulty. However, the long-term recycle to pyrolysis requires additional study, since temperatures are rather low and there is no basis on which to estimate the degree of "bypass" through the fluidized bed system. The question may be largely academic, however, because it would appear that a large-scale installation, unless it were arranged to combust char locally, would include some form of high-temperature char gasification. We have assumed that pyrolysis liquor may be recycled in our design.

Facilities required to treat water, including raw water, boiler feed water, and aqueous effluents, will include the following separate collection facilities:

- Effluent or chemical sewer
- Oily water sewer
- Oily storm sewer
- Clean storm sewer
- Cooling tower blowdown
- Boiler blowdown
- Sanitary waste

Retention ponds for runoffs and for flow equalization within the system will be required. Runoff from the paved process area could easily exceed 15,000 gpm during rainstorms. Runoff from the unpaved process and storage areas could exceed 80,000 gpm in a maximum 1-hour period.

Pretreatment facilities will include sour water stripping for chemical effluents and Imhoff tanks or septic tanks and drainage fields for sanitary waste.

Gravity settling facilities for oily wastes will include API separators, skim ponds, or parallel plate separators.

Secondary treatment for oily and chemical wastes will include dissolved air-flotation units, granular-media filtration, or chemical flocculation units.

Oxygen demand reduction may be accomplished in activated sludge units, trickling filters, natural or aerated lagoons, or by activated carbon treatment.

Boiler feedwater treatment will in general involve use of ion-exchange resins. Reverse osmosis, electrodialysis, and ozonation may find special application.

Evaporation will of course occur throughout this system, and the concern of the designers will be to limit the coevolution of noxious or undesirable components which may be present. We note that it may be necessary to cover portions of the watertreatment facility and/or provide forced draft over some units to avoid undue discharge of hydrocarbons into the atmosphere. In the latter case, as with direct oxidation or ozonation, sweep gases would be ducted to an incinerator or boiler, and provisions for minimizing explosive hazard would be required.

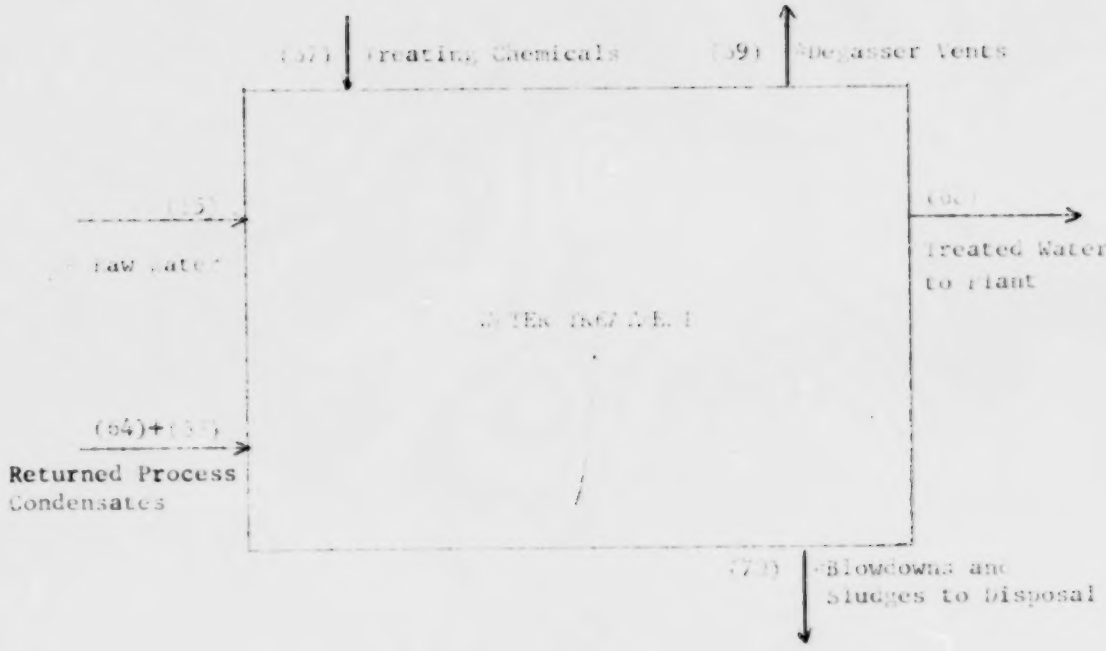


Figure 30

Water Treatment

Table 33

Water Treating

Inlet Streams:

*(65) Raw Water Makeup; 7600 gpm. Complete water analysis per Table 35.

(64)(66) Returned process condensates; 3000 gpm.

(67) Water Treatment chemicals, including pebbled quicklime, sodium hydroxide solution, sulfuric acid, alum, polymer solution, chlorine, hypochlorite, demineralizer and zeolite polymers, salt, anthracite filter media.

Outlet Streams:

(68) Treated Water to Users; 10,600 gpm.

*(69) Vents from condensate degassers. To be analyzed for trace constituents per Table 35.

*(70) Blowdowns and chemical sludges to disposal. To be analyzed for trace sulfur compounds and trace elements per Table 35. May require special treatment.

* Analytical Samples.

4.15 Cooling Water (Figure 31 and Table 34)

A total of 200,000 gpm of cooling water is indicated to be required for operating the FMC design. Because most of this requirement is used for thermal exchange against relatively low-pressure streams, the circuit should be relatively free from process contamination leakage.

A design wet bulb temperature of 77°F and an approach to the wet bulb temperature of 8°F was assumed, with a circulating water temperature rise of 30°F. 9,000 gpm is required as cooling tower make-up, equivalent to 4.5 percent of circulation. Some 3,000,000 pounds per hour of water is evaporated at the cooling tower, 600 gpm is lost as drift, and 2400 gpm is withdrawn as blowdown and is directed to the water treatment facility.

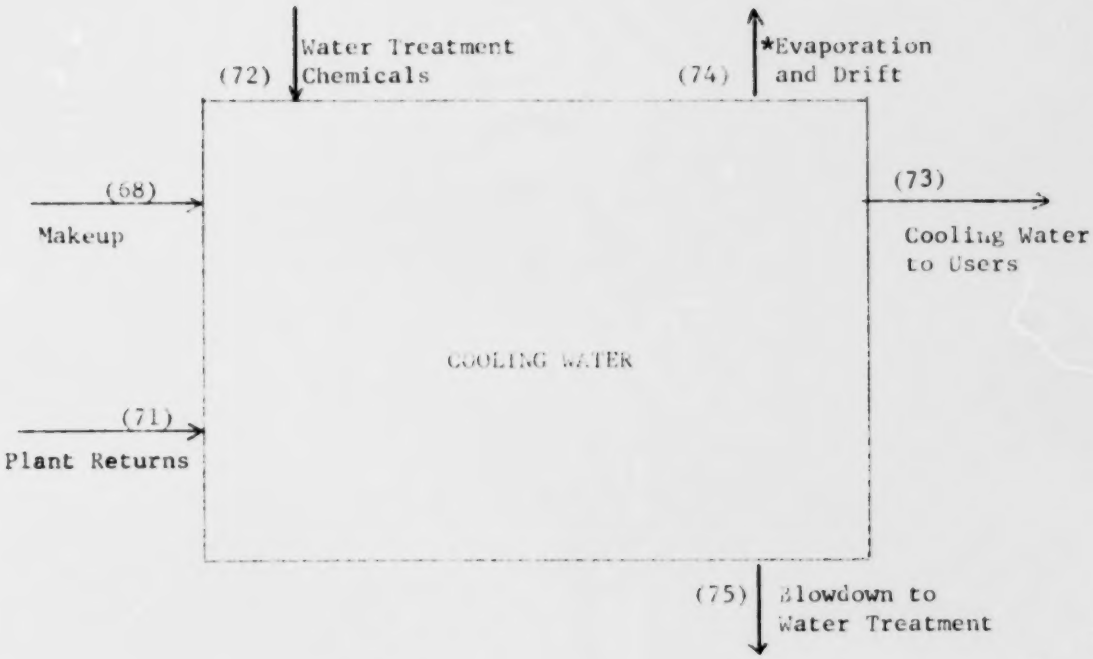


Figure 31

Cooling Water

Table 34

Cooling Water

Inlet Streams:

(68) Makeup Water from Water Treatment; 9000 gpm.

(71) Plant returns; 200,000 gpm.

(72) Water Treatment chemicals including anti-foam package, biological (growth control) package, inhibitor feed package, pH (sulfuric acid) package.

Outlet Streams:

(73) Cooling water to users; 200,000 gpm.

*(74) Evaporation from Towers; 6000 gpm and Drift from Towers; 600 gpm. Atmosphere downwind of towers to be analyzed for trace constituents per Table 35.

(75) Blowdown to Water Treatment; 2400 gpm.

* Analytical Sample.

4.16 Process Analytical Summary

The streams indicated for analysis around the COED Process model are summarized in Table 35, along with specific references to suggested sampling and analytical procedures described in the Analytical Sections 5-9.

The qualifications applicable to the analytical scheme for coal gasification described in Section 3.18 are likewise applicable to the liquefaction scheme. We note again that coal liquefaction encompasses a much wider variety of processing alternatives than does gasification, and that the processing sequence in a particular "liquefaction" system may differ considerably from the COED system. However, the integrated facility, when broken down into unit operations in the manner presented herein, will be found to differ generally only in the relative sizes and sequence of such operations, with special differences occurring mainly in the reactor module.

Table 35

Summary of Effluent Streams to be Analyzed for COED Plant

COAL LIQUEFACTION

COED PROCESS MODEL

Stream No.	Stream Name	Analysis For	Analytical Section Reference
5	Dust and Fumes in Coal Preparation Area	Atmosphere in enclosed spaces, discrete stack emissions from enclosed spaces and from dust collection equipment, and atmosphere in vicinity of coal piles, open conveying and handling equipment, and coal fines collection system to be analyzed for particulates.	Total particulates to be determined in enclosed spaces using a high volume sampler, Section 9; in stacks using EPA Method No. 5, Section 9; and the ASTM D 1739 dust fall test will be performed at various site locations.
6	Sized Coal to Pyrolysis	Complete coal analysis including trace elements.	Coal will be analyzed for the elements listed in Section 7, Table VI and will be analyzed to determine its gross composition as indicated in Section 7, Table VII.
7	Coal Dryer Vent Gas	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO_2/SO_3, NO_x, CO, CO_2, COS, H_2S, and CH_3SH and for particulates. Refer to Section 9.
11	Purge Gas from Stage 1 Pyrolysis	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO_2/SO_3, NO_x, CO, CO_2, COS, H_2S, and CH_3SH and for particulates. Refer to Section 9.
20	Product Char	Complete Coal Analysis Including Trace Elements	Coal will be analyzed for the elements listed in Section 7, Table VI and will be analyzed to determine its gross composition as indicated in Section 7, Table VII.
22	Stack Gas from Superheaters	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO_2/SO_3, NO_x, CO, CO_2, COS, H_2S, and CH_3SH and for particulates. Refer to Section 9.

Table 35 (Cont'd)

Summary of Effluent Streams to be Analyzed for COED Plant

COAL LIQUEFACTION

COED PROCESS MODEL

Stream No.	Stream Name	Analysis For	Analytical Section Reference
26	Stack Gas from Transport Gas Heater	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO_2/SO_3, NO_x, CO, CO_2, COS, H_2S, and CH_3SH and for particulates. Refer to Section 9.
35	Stack Gas From Preheater	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO_2/SO_3, NO_x, CO, CO_2, COS, H_2S, and CH_3SH and for particulates. Refer to Section 9.
38	Hydrotreating Reactor Coke Product	Complete Coal Analysis Including Trace Elements	Coke will be analyzed for the elements listed in Section 7, Table VI and will be analyzed to determine its gross composition as indicated in Section 7, Table VII.
40	Syncrude Product	Sulfur Trace Elements	This stream will be analyzed for the metals listed in Section 8, Table VIII and for total sulfur as indicated in Section 8, Table X.
47	Benfield Blowdown	Complete coal solids analysis and complete water analysis.	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV. The high K_2CO_3 and $KHCO_3$ content of this stream may cause interferences in the analyses.

Table 35 (Cont'd)

Summary of Effluent Streams to be Analyzed for COED Plant

COAL LIQUEFACTION

COED PROCESS MODEL

Stream No.	Stream Name	Analysis For	Analytical Section Reference
50	Stack Gas from Hydrogen Plant Heaters	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO_2/SO_3, NO_x, CO, CO_2, COS, H_2S, and CH_3SH and for particulates. Refer to Section 9.
52	Separated CO_2 from Reformed Stream	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gas will be analyzed for SO_2/SO_3, NO_x, CO, CO_2, COS, H_2S, and CH_3SH and for particulates. Refer to Section 9.
55	Sulfur Product	Trace Elements	Sulfur will be analyzed for the metals listed in Section 8, Table VIII, by adaptation of methods which were designed for oil analysis.
56	Stretford Blowdown	Complete coal solids analysis and complete water analysis.	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV. The Na, V, and carbonate content of the stream may cause interferences in the analyses.
57	Sulfur Plant Off Gas	Trace Sulfur Compounds Particulates (V, Na)	Off-gases to be analyzed for particulates and for COS, H_2S, CH_3SH and SO_2/SO_3, see Section 9. In addition Na and V will be determined on particulates, see Section 7.
61	Boiler Stacks and Heaters (Multiple Stacks are Involved)	Stack Gas Analysis Trace Sulfur Compounds Particulates	The stack gases will be analyzed for SO_2/SO_3, NO_x, CO, CO_2, COS, H_2S and CH_3SH and for particulates. Refer to Section 9.

Table 35 (Cont'd)

Summary of Effluent Streams to be Analyzed for COED Plant

COAL LIQUEFACTION

COED PROCESS MODEL

Stream No.	Stream Name	Analysis For	Analytical Section Reference
62	Lime Sludge From Flue-Gas Treatment	Complete coal solids analysis and complete water analysis.	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV. The high Ca content of the stream may cause interferences in the analyses.
63	Char Ash from Boilers	Complete coal solids analysis and complete water analysis.	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV.
65	Raw Water to Process	Complete Water Analysis	Raw water will be analyzed for all components listed in Section 6, Table IV.
69	Degasser Vent Gases	Trace Sulfur Compounds Hydrocarbons	Vent gases will be analyzed for Thiophene, CO_2, SO_2/SO_3, COS, H_2S, and CH_3SH and for benzene, toluene, and other volatile organics See Section 9.
70	Sludges from Water Treatment	Complete coal solids analysis and complete water analysis.	The solid material will be analyzed for the components listed in Section 7, Tables VI and VII. The aqueous phase will be analyzed for the components listed in Section 6, Table IV. The chemicals used for water treatment may cause interferences in the analyses.
74	Evaporation and Drift from Cooling Towers	Atmosphere in vicinity of cooling towers to be sampled for: Trace Sulfur Compounds Trace Elements Hydrocarbons and PNA	A high volume sample will be collected and the particulates will be analyzed for the metals listed in Section 7, Table VI. In addition the atmosphere will be sampled for benzene, toluene and other volatile organics; polynuclear aromatics; and for thiophene, CS_2, SO_2/SO_3, COS, H_2S, and CH_3SH (Section 9).

4.17 Unit Material Balances

As indicated for gasification in Section 3.19 above, further analyses may be necessary if an over-all plant balance cannot be made using analyses of streams in table 35. Additional streams are listed below for critical units.

Coal Preparation - Streams 2 and 4.

Stages 2,3,4 Pyrolysis - Streams 13, 14, 15, 16, 17, 18, 19, 21, 22, and 39.

Oil Filtration - Streams 25, 27, 28, 29, 30 and 31.

Hydrotreating - Streams 30, 32, 33, 34, 36, 37, and 39.

Sulfur Recovery - 45 and 51, 53 and 54.

Power and Steam Generation - 30, 46, 58, 59, 60 and 64.

Cooling Water - Streams 68, 71, 72, 73 and 75.

The above would require 37 to 38 more streams to be analyzed than the 23 listed in Table 35.

As indicated under Gasification (in 3.19.8), it may be necessary in some cases to make heat and material (including potential pollutants) balances around a particular unit. An example might be Oil Filtration (Section 4.7). Although no streams are indicated to be analyzed to make a pollutant material balance around the plant, it may be desirable to compare the pollution load of filtration with, for example, distillation. All streams of figure 23, together with any other streams of the particular unit of interest, would be sampled and analyzed according to the analytical sections of this plan and these analyses, together with utility requirements, would allow this unit to be compared with other units from the viewpoint of environmental impact.

5. TYPICAL AVAILABLE STREAM ANALYSES AND STANDARDS

Tables 36-39 list some stream analyses for existing commercial plants, proposed plants and pilot plants for those materials that have been suggested in the Analytical Test Plan. In some cases the rules were "bent" to include some data that shows approximate results. For example, results on benzene soluble tar from the Synthane process were included. Similarily, data from a biox unit at SASOL were included even though streams from other industries were mixed with the Sasol stream before the biox unit.

Also included in table 36 are data ranges for analysis of U.S. coals. To indicate ranges of interest, information has been included on existing or proposed state and Federal standards for air and water effluents.

It is obvious that data on most streams of interest are not available and even for those streams about which something is known, much of the data is lacking.

Table 40 presents some standards for water effluents and table 41 presents some air standards. These tables give some indication of what is or will be needed in the way of stream analyses and show something of the ranges of components to be analyzed.

Table 16

Stream Analyses for Existing Plants, Coal

Stream No. From Analytical Test Plan — 5 (Gasification ; 6 (Liquefaction)

Stream Identification	Sized Coal to Gasifiers and Liquefaction, ppm						
	EPNG (Ref. 1) Navajo Coal	Synthane (Ref. 43) Illinois No. 6	Westfield (Ref. 44)	SASOL (Ref. 45)	SRC (Ref. 47) Illinois No. 6	COED (Ref. 39) Illinois No. 6	U.S. Coals From Ref. 42
Stream Analyses							
As	0.1-3	---	---	2-5	19	---	3-60
Ba	---	---	---	---	50	---	---
Be	---	---	---	2-3	<10	---	0.08-11
Ca	---	---	---	---	3400-4800	---	---
Cd	0.2-0.4	---	---	<0.1	1.5- 33	---	---
Cr	---	---	---	---	---	---	2.7-20
F	200-780	---	---	100	300	---	10-100
Fe	---	---	---	---	20,000-24,000	---	---
Hg	0.2-0.35	---	---	<0.1	0.05	---	0.01-1.2
Li	---	---	---	---	7.4	---	---
Mn	---	---	---	500	39-75	---	---
Na	---	---	---	---	166-320	---	---
Ni	3-30	---	---	30-50	29-120	---	1-50
Pb	1.4-4	---	---	10-20	8-10	---	6-33
Sb	0.3-1.20	---	---	<0.5	10.6	---	---
Se	0.08-0.21	---	---	---	7	---	0.5-4.0
V	---	---	---	300-500	200	---	2.3-190
Fixed C, %	---	43	---	---	51.70	51.1 (Dry)	---
Volatile Matter, %	---	37.5	---	---	38.47	37.2 (Dry)	---
Ash, %	17.3	11.2	13.24	31.6 (Dry)	7.13	11.6 (Dry)	---
Moisture, %	16.5	8.3	16.5	8	2.7(After drying)	12.6	---
C, % MAF	76.72	63	56.52	52.4	70.75	66.9	---
H, % MAF	5.71	.3	3.73	2.6	4.69	4.9	---
N, % MAF	1.37	1.1	0.89	1.2	1.07	1.1	---
S, % MAF	0.95	3.5	1.13	0.4	3.38	4.1	---
O, % MAF	15.21	15.9	7.99	11.7	10.28	11.7	---
P, % MAF	---	---	---	---	---	---	---
Calorific Value, Btu/lb	7,500-10,250	---	9,810	8,890	12,821	12,420	---
Fusibility of Ash, °C							
Softening Point	---	---	---	1375	---	---	---
Melting Point	---	---	---	1475	---	---	---
Fluid Point	---	---	---	1500	---	---	---

Table 37

Stream Analyses for Existing Plants,
Liquid Organic Products

(ppm except as noted)

Stream No. from ATP	17 (Gasification)			24 (Gasification)		30 (Gasification)	
	Coal Tar			Tar Oil, ppm		Naphtha, ppm	
Stream Identification	Synthane (Ref. 43) (Benzene Soluble)	Westfield (Ref. 44)	SASOL (Ref. 43)	Westfield (Ref. 43)	SASOL (Ref. 45)	Westfie'd (Ref. 43)	SASOL (Ref. 45)
Stream Analyses							
As	0.7	---	3.1-5.0	---	23-30	---	---
Ba	---	---	---	---	---	---	---
Be	---	---	0.6-1.0	---	0.06	---	---
Ca	---	---	---	---	---	---	---
Cd	---	---	0.03- 0.05	---	0.3	---	---
Cr	---	---	---	---	---	---	---
Fe	---	---	--- ---	---	---	---	---
Hg	---	---	0.3-0.5	---	0.1-0.15	---	---
Li	---	---	--- -	---	---	---	---
Mn	---	---	1.6-4.1	---	0.2-0.3	---	---
Na	---	---	---	---	---	---	---
Ni	---	---	1.6-4.1	---	1-1.4	---	---
Pb	---	---	50	---	0.5-1.2	---	---
Sb	---	---	0.8-1.0	---	0.5-0.6	---	---
Se	---	---	---	---	---	---	---
V	---	---	1.8-8.2	---	0.1-0.3	---	---
TOTAL S, %	2.8	0.77	0.3	0.29	0.25	0.078	0.34

Table 38

STREAM ANALYSIS FOR EXISTING PLANTS, ASH

Stream No. from Analytical Test Plan 67 (Gasification)

Stream Identification	Wet Ash (Dry Basis), ppm Westfield (44)	SASOL (44) (Not Quenched)	Azot Sanayii (47) (Not Quenched)
Stream Analysis			
As	---	1-2	---
Ba	---	---	---
Be	---	<0.5	---
Ca	25,600	50,000	43,000-71,000
Cd	---	<0.1	---
Cr	Trace	---	---
F	---	150	---
Fe	32,900	35,000	91,000-105,000
Hg	---	<0.1	---
Li	---	---	---
Mn	Trace	2,000	---
Na	---	5,000	2,200-7400
Ni	Trace	150-200	---
Pb	---	50	---
Sb	---	<0.5	---
Se	---	---	---
V	---	1000	---

Table 39

Stream Analyses for Existing Plants, Water Effluent

Stream No. from Analytical Test Plan 39 (Gasification) and others

Stream Identification	Biox Unit Treated Water Effluent From SASOL (45) mg/l where applicable
Stream Materials	
pH	8.5
Suspended solids	31.0
TDS	959
Free and saline ammonia (as N)	7.45
As	0.05
B	4.40
Hexavalent Cr	----
Total Cr	0.01
Cu	0.04
Phenols (Steam volatile)	0.03
Pb	0.02
CN^-	0.11
$S^=$	----
F^-	5.87
Zn	0.07
Na	158
Phosphates (as P)	0.29
COD	82
OA	11
Soap, Oil and Grease	0.13
Fe	----
Cd	----
Mn	----
Ag	----
Nitrates, total	----
, As NO_2	----
, As NH_3	----
Phosphates, Max.	----
, Average	----
Dissolved Oxygen	----
Max. T. °F	----
Max. ΔT, °F	----
Turbidity, Max Δ JTV	----
BOD_5	----
TOC	----

Table 40

Standards for Water Effluents

Stream Materials	States, Existing and New (Ref. 48) mg/l where applicable	Proposed New Standards for Petroleum Refining (Ref. 50) lb/1000 bbl (≅lb/6,500 M Btu) 30 Day Max. Range	One Day Max Range
pH	(4.3-7.0)-(8.0-10.0)	6.0-9.0	6.0-9.0
Suspended	----	0.93-4.2	1.2-5.2
TDS	----	----	----
* and saline		----	----
Ammonia (as N)	----	0.3-2.6	0.4-3.4
As	All toxics:	----	----
B	0.00-0.50	----	----
Hexavalent Cr	0.05-0.5	0.00046-0.0021	0.00058-0.0026
Total Cr	0.05-1.0	0.023-0.106	0.030-0.132
Cu	0.005-1.0	----	----
Phenols (Steam volatile)	----	0.0099-0.046	0.014-0.065
Pb	0.05-0.10	----	----
CN^-	----	----	----
$S^=$	----	0.0081-0.038	0.013-0.059
F^-	----	----	----
Zn	0.1-5.0	0.046-0.16	0.058-0.21
Na	----	----	----
Phosphates (as P)	----	----	----
COD	----	5.3-48.2	6.6-60.2
OA	----	----	----
Soap, Oil and Grease	----	0.46-2.1	0.58-2.6
Fe	0.1-1.5	----	----
Cd	0.1-0.5	----	----
Mn	0.05-1.0	----	----
Ag	0.0005-0.05	----	----
Nitrates, total	0.4-45.0	----	----
, As NO_2	5.0-50.0	----	----
, As NH_3	0.01-5.0	----	----
Phosphates, Max.	1.0-4.0	----	----
, Average	.025-0.1	----	----
Dissolved Oxygen	2.0-6.0	----	----
Max, T. °F	66-96.8	----	----
Max, ΔT, °F	0-20	----	----
Turbidity, Max Δ JT	5-50	----	----
BOD_5	----	1.5-6.6	1.85-8.2
TOC	----	1.3-9.2	1.6-11.4

Table 41

Air Standards

	Fuel Burning Equipment (Ref. 48) States Ranges (Existing or All)	Industrial (Ref. 48) States Ranges (Existing or All)	Selected New Source Performance Standards for Specific Sources (Ref. 50,51) Steam Generators	Petroleum Refining Cat Cracker	State of New Mexico Emissions for Coal Gasification Plants (Ref. 46) Gas-Fired Power Plant for Gasification Plants	Gasification Plants
Particulates, lb/10^6 Btu			0.10	0.027 gr/dscf +0.10 lb/10^6 MM Btu max. fuel	0.03	0.03 gr/dscf
5,000 Btu/hr*	0.02+-0.6	N.A.	(Btu input)			
10,000 Btu/hr*	0.02+0.6	N.A.	(20% Opacity)			
20,000 Btu/hr*	0.02+0.6	N.A.		30% opacity except 3 min./hr.		
Process Rate, lb/hr.						H_2S - 10 ppm Total Sulfur - 0.008 lb/MM Btu H_2S + COS + CS_2 - 100 ppm HCN - 10 ppm HCl - 5 ppm NH_3 - 25 ppm
200 tph	N.A.	21.20 - 142.7	N.A.	--		
500 tph	N.A.	31.20 - 261.60	N.A.	--		
1000 tph	N.A.	21.20 - 419.6	N.A.	--		
Sulfur Oxides, lb/10^6 Btu	(For Solid Fuel) 0.8 - 6.0 (For Liquid Fuel) 0.3 - 1.5	N.A. N.A.	(For Solid Fuel) 1.2 (For Liquid Fuel) 0.8	0.10 gr H_2S/dscf in fuel gas --	0.16	
Sulfur Oxides, ppm	N.A.	800 - 2000	N.A.	N.A.	N.A.	
Nitrogen Oxides, lb/10^6 Btu	(Solid Fuel) 0.3 - 1.8 (Liquid Fuel) 0.30 - 0.60 (Gaseous Fuel) 0.20 - 0.60	N.A. N.A. N.A.	(Solid Fuel) 0.7 (Liquid Fuel) 0.3 (Gaseous Fuel) 0.2	-- --	0.20	
Carbon Monoxide	200 ppm (1 entry)	200 ppm (1 entry) 40 mg/m^3 - 1 hr. Average Concentration		0.05 v% for cat cracker		

N.A. -- Not Applicable

* 1 MM Btu/hr ≈ 1 tpd of coal

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7. ANALYTICAL CONSIDERATIONS

7.1 Introduction

In selecting the possible pollutants for analysis in the selected plant streams, five factors were considered. These were 1) the potential impact of pollutant on the environment, 2) available data regarding the composition of commercial coal gasification and liquefaction plant streams, 3) the minor and trace constituents of coals, 4) various process considerations, and 5) lists supplied by the EPA of materials which are considered environmental hazards. Some of the literature which was consulted to arrive at the selection of possible pollutants is given in Table I.

On the basis of this literature, the materials listed in Table II were selected for analysis. In addition to these materials, additional analyses were deemed desirable to include in the test plan because some environmental insight might be gained into the process in general; these analyses are listed in Table III.

Many analytical procedures are potentially applicable for the analysis of the potential pollutants and other required measurements, listed in Tables II and III, in the various streams of the liquefaction and gasification plants. In selecting the suggested procedures, which are given later, consideration was given to 1) procedures which are widely used for analysis of the pollutants in a given matrix, 2) procedures which have been demonstrated to be applicable for determinations of certain components of a given matrix, 3) procedures which are potentially applicable for the analysis of a matrix component but have not been extensively tested, 4) procedures for multicomponent analysis, and 5) the concentration ranges at which the procedures are applicable.

It must be stressed that since the detailed compositions of the plant streams are unknown, components may be present which will interfere with the suggested procedures. If interferences are suspected during the course of analysis for a pollutant or if a small quantity of a pollutant is to be measured in the presence of a large quantity of another component, the applicability of the procedure should be determined.

It is to be noted that the literature is frequently contradictory as to the applicability of procedures to various components and procedures other than the suggested procedures are available for measurement of pollutants. If an alternative procedure is selected, its applicability should be evaluated.

It is convenient to broadly classify the types of samples to be obtained from plant streams into 1) aqueous samples, 2) coal and coal-related solid samples, 3) gas and ambient air samples, and 4) coal liquid samples. The analytical methods which are suggested for samples

TABLE I

LITERATURE SURVEYED FOR SELECTION OF POSSIBLE POLLUTANTS

"Occurrence and Distribution of Potentially Volatile Trace Elements in Coal," R. R. Kuch, H. J. Gluskoter and N. F. Shimp, Illinois State Geological Survey, EPA-650/2-74-054, July 1974.

"Potential Pollutants in Fossil Fuels," E. M. Magee, H. J. Hall, and G. M. Varga, Jr, EPA-R2-73-249, June 1973.

"Liquid Coal Compositional Analysis by Mass Spectrometry," J. T. Swansiger, F. E. Dickson, and H. T. Best, Anal. Chem., 46, 730 (1974).

"Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Gasification, Section 3, Lurgi Process," H. Shaw and E. M. Magee, EPA-650/2-74-009-c, July 1974.

"Evaluation of Pollution Control in Fossil Fuel Conversion Processes, Liquefaction, Section 1, COED Process," C. D. Kalfadelis and E. M. Magee, EPA-650/2-74-009-e, February 1975.

TABLE II

POSSIBLE POLLUTANTS FROM COAL PROCESSING

Metals	Gases	Polynuclear Aromatics
As	AsH_3	benzo(k)fluoranthene
Ba	H_2Se	Benzo(b)fluoranthene
Be	Fe, Co and Ni Carbonyls	Benzo(a)pyrene
Ca	SO_2/SO_3	Benzo(e)pyrene
Cd	NO_x	Perylene
Cr	COS	Benzo(ghi)perylene
Fe	H_2S	Coronene
Hg	CH_3SH	Chrysene
Li	NH_3	Fluoranthene
Mn	H_2	Pyrene
Na		Benzo(ghi)fluoranthene
Ni		Benz(a) anthracene
Pb	CO	Triphenylene
Sb	CO_2	Benzo(j)fluoranthene
Se		
V	CH_4	

Other Organic Materials

Thiophene
CS_2
phenols
benzene
toluene
xylene
oil
acids
aldehydes

Inorganic Ions

CN^-
SCN^-
F^-
$S^=$
$CO_3^=$
Cl^-
Phosphates

Particulates

TABLE III

OTHER ANALYSIS

Coal Analysis

Moisture
Ash
Volatile Matter
Fixed C
S
P
C
H
N
Calorific Value
Fusibility of Ash

Water Quality Indicators

Specific Conductance
pH
COD
BOD
TOC
Residue
Dissolved Oxygen
Suspended solids
Dissolved solids
Turbidity
Color
Oils

are discussed separately, as are sampling and preservation of samples, for each sample type. Before these specific discussions, a general discussion on the analysis samples for metals is presented because of the rapidly developing technology in this area and the fact that many different analytical techniques are potentially applicable for metals analysis.

7.2 Analysis of Metals

Much attention has recently been given to the analysis of metals in aqueous, oil, coal, and particulate samples. Flame atomic adsorption and heated vaporization atomic absorption have been widely used for analysis of samples containing small quantities of metals due to the selectivity and high sensitivity of the techniques and to the relatively low cost of the instrumentation involved. Neutron activation, spark source mass spectrographic, and emission spectrographic techniques have been applied for multielement trace analysis. X-ray fluorescence has been widely applied for metal analysis at somewhat higher levels than the aforementioned techniques.

The accurate analysis of trace quantities of metals in coal, coal ash, petroleum, and petroleum products has been the subject of much investigation recently. The National Bureau of Standards supplied samples of coal, fly ash, fuel oil, and gasoline to cooperating laboratories for analysis of trace metals as part of a program to 1) assess the need for standard reference materials of these substances, and 2) to determine comparability of various analytical techniques. The results obtained on these samples (1,2) indicated that there is definitely a need for standard reference materials of these substances because of the scatter in the results which were reported.

The Illinois Geological Survey recently published the results of a study of the determination of trace elements in coal using a variety of analytical techniques and found that certain techniques were better suited than others for the analysis of certain elements in coal.

The need for methods to obtain accurate, reliable data on trace metals content on oils is reflected in the fact that a project involving five petroleum companies was formed to develop and evaluate the precision and accuracy of methods for the analysis of petroleum oils for metals at the 10 ng/g level. The undertaking was deemed to be of such significance that when the first publication from the project appeared in Analytical Chemistry, an editorial regarding the project appeared in the same issue (3).

The point of this discussion is that perhaps the greatest difficulty and uncertainty in the analysis of the liquefaction and gasification plant streams will probably be with regard to their metals content. Therefore particular attention should be given to the implementation of the suggested procedure in the laboratory. Experiments should be performed to validate and develop the techniques that are needed for the use of the procedures before the analysis of the plant streams commences.

7.3 Alternative Analytical Techniques

References have been provided, when applicable, for alternative analytical techniques. For example, three sources have been cited for analysis of aqueous samples (Section 6.1). What is believed to be the best techniques have been selected for use in this analytical test plan. These selections were made on the basis of (1) use experience in a number of laboratories, (2) validation by independent workers, (3) methods used by EPA, and (4) use experience in analyses of related materials. As indicated above, the use of an alternative procedure found in the references should be validated.

7.4 Results Analysis

Since the overall objective of the test plan is to provide a material balance of all possible pollutants from a given plant, it is necessary that the analyses be sufficiently accurate to give the desired accuracy in the balance. The references cited indicate the number of samples to be analyzed in each case. This should provide sufficient accuracy for the desired result. In cases where a material balance is not obtained, a detailed search must be made as to the cause of the imbalance. This cause may not be related to the sampling and analysis but may be caused by other factors such as errors in the estimate of the delay time between process changes and attainment of steady state conditions down stream. Another factor may be reactions of a stream component between the unit where it is formed to the unit where the sampling is made. (Bacterial action in cooling towers was previously pointed out as an example of this problem.) Another problem source is the possibility of adsorption or absorption and desorption of trace materials when process conditions are changed. For instance, in acid gas treatment, if a trace component concentration is increased due to changes in a gasification reactor variable, the effluent from the acid gas absorbers will not contain the steady state concentration of that component until the absortion solution is saturated with that component at its new partial pressure. Changes in temperature of operating units can have similar effects. The age of absorber or catalysts can also produce these anomalous results.

Unless otherwise indicated, the following procedure is recommended to check sampling and analysis techniques: When a stream is to be analyzed for the first time, five samples should be taken. Three of these should be submitted for analysis as is. The other two should be spiked with two different levels of the component(s) of interest. In this way, if the final analyses correctly show the effects of spiking as well as agreement of the unspiked analyses, then additional validity of the results is indicated.

A final word of caution should be injected as to the analysis of the results. This has to do with sampling streams where the act of sampling can change the concentration of the stream components. This is often the case when sampling high temperature streams. Unless the sample is cooled extremely rapidly, a shift in equilibrium of the components can take place and reactions can take place on the sampler walls.

In most cases of interest, samples can be taken from two or more cool streams to give the desired information (e.g., a cool gas sample and a condensed water sample may take the place of a hot sample containing water vapor). Again, in all cases, experience and technical judgement are necessary to produce reliable results.

8. ANALYSIS OF AQUEOUS SAMPLES

8.1 Introduction

There are three collections of procedures for the analysis of aqueous samples for pollutants which are in general use in this country. These are "Methods for Chemical Analysis of Water and Wastes," EPA-625-/6-74-003, Environmental Protection Agency, Washington, D.C., 1974; "Standards Methods for the Examination of Water and Waste Water," 13th Ed., American Public Health Association, Washington, D.C. 1971; and "Annual Book of ASTM Standards, Part 31, Water," American Society for Testing and Materials, Philadelphia, Pa., 1974. These are abbreviated EPA/74, W & WW/13, and ASTM/31, respectively in this section. In addition to these collections, the chemical literature was surveyed for methods which are applicable for the analysis of pollutants in waters.

In selecting the suggested procedures which are given in Table IV, primary consideration was given to the methods in EPA/74 since the procedures in this collection will be used by the agency in determining compliance with water and effluent standards established by the agency. Where these methods were not thought to be applicable or where methods did not exist for potential pollutants of interest, other procedures were chosen.

For the analysis of metals as a group, neutron activation, spark source mass spectrographic and emission spectrographic techniques have been used. If a simultaneous determination of metals is desired, consideration should be given to the technique of LeRoy and Lincoln (4) which was shown to be applicable to the simultaneous determination of 36 elements, including all of those listed in Table II, except Ba, Li, and Se.

The methods in Table IV may be used to measure both total and dissolved constituents of samples. If the dissolved concentration is to be determined, the sample is filtered through a 0.45 µm membrane filter and the filtrate analyzed by the suggested procedure. Filtration in the field is recommended; if that is not feasible, the sample should be filtered as soon as it is returned to the laboratory.

8.2 Sampling

Sampling methods which are generally applicable to industrial waters are discussed in detail in ASTM D-510 and the use of one of these procedures is recommended. Apparatus, frequency, and duration of sampling, composite samples, sampling points, and preparation of sample bottles are discussed in ASTM D-510.

8.3 Preservation of Samples

The amount of sample that should be collected for the analysis of each component, the method of preservation and the holding time before analysis, where these factors have been reported, are given in Table V. More information regarding these factors is discussed in many of the suggested methods.

TABLE IVa

SUGGESTED ANALYTICAL METHODS FOR AQUEOUS SAMPLES

Component or Measurement	Method	Suggested Range[A] of Method
Phenol	EPA/74, 32730	5 - 1000 µg/l
Ammonia	EPA/74, 00610	0.05 - 1.0 mg/l
Sulfide	EPA/74, 00745 (W&WW/13, 228)	>1 mg/l
Oil and grease	EPA/74, 00550, 00556 or 00560	>0.2 mg/l
Cyanide, total	EPA/74, 00720	>0.02 mg/l
Carbon dioxide	W&WW/13, 111	see method
Acids, volatile	W&WW/13, 233	up to 5,000 mg/l
Conductance, specific	EPA/74, 00095 (W&WW/13, 154)	see method
pH	EPA/74, 00400	
Fluoride, total	EPA/74, 00951	oil - 100 mg/l
Oxygen demand, chemical	EPA/74, 00335	5 - 50 mg/l
Chloride	EPA/74, 00940	"all ranges"
	(ASTM/31 D-512 Ref. Method A)	
Residue, total filterable	EPA/74, 70300	10 - 20,000 mg/l
Residue, total nonfilterable	EPA/74, 00530	10 - 20,000 mg/l
Phosphorus, total	EPA/74, 00665	0.01 - 0.5 mg P/l
Oxygen, dissolved	EPA/74, 00299	>0.05 mg/l
Metals by Atomic Absorption		
Antimony	EPA/74, 01097	1 - 40 mg/l
Arsenic	EPA/74, 01002	>2 µg/l
Barium	EPA/74, 01007	1-2 mg/l
Beryllium	EPA/74, 01012	0.05 - 2 mg/l
Cadmium	EPA/74, 01027	0.05 - 2 mg/l
Calcium	EPA/74, 00916	0.2 - 20 mg/l
Chromium	EPA/74, 01034	0.2 - 20 mg/l
Iron	EPA/74, 01045	0.3 - 10 mg/l
Lead	EPA/74, 01051	1 - 20 mg/l
Lithium	← Applicability to be determined →	
Manganese	EPA/74, 01055	0.1 - 10 mg/l
Mercury	EPA/74, 71900	>0.2 µg Hg/l
Nickel	EPA/74, 01067	0.3 - 10 mg/l
Selenium	EPA/74, 01147	2 - 20 µg/l
Sodium	EPA/74, 00929	0.03 - 1.0 mg/l
Vanadium	EPA/74, 01087	1 - 100 mg/l
Organic Carbon, total	EPA/74, 00680	>1 mg/l
Oxygen Demand, Biochemical	EPA/74, 00310 (W&WW/13, 220)	see method
Trihalomethane	J. M. Bruce and N. G. Bevan, Anal. Chem., 25, 449 (1953)	0.5 - 20 mg/l
Nitrate	EPA/74, 00620	0.1 - 2 mg NO_3 (as N)/l
Sulfate	EPA/74, 00740 (W&WW/13, 158)	detection limit is 3 mg $SO_3^=$/l

[A] Range may be extended upward by appropriate dilutions in many instances; refer to the method.

TABLE IVb

PRINCIPLES OF THE SUGGESTED ANALYTICAL METHODS

Phenol EPA/74, 32730, p. 241

Distillation of the sample and reaction of the phenolic compounds in the distillate with 4-aminoantipyrine to form a colored dye. The intensity of the color produced in a function of the phenolic content of the sample.

Ammonia EPA/74, 00610, p. 159

Distillation from a buffer and colorimetric or titrimetric determination of ammonia in the distillate.

Sulfide EPA/74, 00745, p. 284 (W&WW, p. 551)

Distillation of sulfide and titration of distillate with iodine/thiosulfate. Sulfite, thiosulfite, and hyphosulfite interfere.

Cyanide, Total EPA/74, 00720, p. 40

Distillation of hydrogen cyanide from the sample and measurement of cyanide in the distillate titrimetrically or colorimetrically.

pH EPA/74, 00400, p. 239

Electrometric measurement.

Fluoride, Total EPA/74, 00951, p. 63

Distillation of the sample and determination of fluoride in the distillate using a selective ion fluoride electrode.

Chemical Oxygen Demand EPA/74, 00335, p. 21

Oxidation of the sample with potassium dichromate and titration of the excess dichromate with standard ferrous ammonium sulfate solution. For chloride contents above 1000 mg/l use EPA/74, 00340, p. 25; minimum accepted COD level for this method is 250 mg/l COD.

Chloride EPA/74, 00940, p. 29 (ASTM/31 D-512, Referee Method A)

Titration with mercuric nitrate.

Residue, Total Filterable EPA/74, 70300, p. 266

Filtration of the sample and evaporation of the filtrate.

TABLE IVb (Cont'd.)

Residue, Total Nonfilterable EPA/74, 00530, p. 268

Filtration of the sample and determination of the residue when dried at 105°C.

Phosphorous, Total EPA/74, 00665, p. 249

Treatment of the sample to convert phosphorus compounds to orthophosphate and determination of orthophosphate by formation of an antimony-phosphomolybdate complex. For determination of orthophosphate in sample use EPA/74, 70507; from determination of total hydrolyzable phosphorus use EPA/74, 00669; and for determination of total organic phorphorus use EPA/74, 00666.

Oxygen, Dissolved EPA/74, 00299, p. 56

Instrumental probes which depend on electrochemical reactions are used.

Carbon Dioxide W&WW/13, 111, p. 86

Nomagraphic and titrimetric methods are discussed.

Acids, Volatile W&WW/13, 233, p. 577

Column chromatography of the sample to separate organic acids and titration of the acids.

Conductance, Specific EPA/74, 00095, p. 275 (W&WW/13, 154, p. 323)

Conductance cell is used.

Metals by Atomic Absorption

Refer to the general discussion on these analyses given in EPA/74 pp. 78-93.

Antimony EPA/74, 01097, p. 94

Lean air-acetylene flame is used.

Arsenic EPA/74, 01002, p. 95

Oxidation of sample followed by arsine generation. Argo./hydrogen/entrained-air flame is used.

Barium EPA/74, 01007, p. 97

Rich nitrous oxide-acetylene flame is used.

TABLE IVb (Cont'd.)

Beryllium EPA/74, 01012, p. 99

Rich nitrous oxide-acetylene flame is used.

Cadmium EPA/74, 01027, p. 101

Oxidizing air-acetylene flame is used.

Calcium EPA/74, 00916, p. 103

Reducing air-acetylene flame is used.

Chromium EPA/74, 01034, p. 107

Slightly rich air-acetylene flame is used.

Iron EPA/74, 01045, p. 110

Oxidizing air-acetylene flame is used.

Lead EPA/74, 01051, p. 112

Slightly oxidizing air-acetylene flame is used.

Lithium

Applicability of atomic absorption to be determined.

Manganese EPA/74, 01055, p. 116

Oxidizing air-acetylene flame is used.

Mercury EPA/74, 71900, p. 118

Sample is oxidized to convert all mercury to the divalent state then divalent mercury is reduced to elemental mercury which is measured by cold-vapor atomic absorption.

Nickel EPA/74, 01067, p. 141

Oxidizing air-acetylene flame is used.

Selenium EPA/74, 01147, p. 145

Sample is oxidized, selenium is reduced to tetravalent state and then converted to hydrogen selenide and measured using an argon/hydrogen/entrained-air flame. Details are given by J. S. Caldwell, E. J. Lishka, and L. F. McFarren, J. Am. Water Works Assoc., 65, 732 (1973).

TABLE IVb (Cont'd.)

Sodium EPA/74, 00929, p. 147

An oxidizing air-acetylene flame is used.

Vanadium EPA/74, 01087, p. 153

A fuel rich nitrous oxide-acetylene flame is used.

Organic Carbon, Total EPA/74, 00680, p. 236

Organic carbon is converted to CO_2 which is measured using an IR detector or is converted to CH_4 and measured using a flame ionization detector.

Oxygen Demand, Biochemical EPA/74, 00310, p. 11 (W&WW/13, 219, p. 489)

The 5-day BOD is an biassay procedure which measures the dissolved oxygen consumed by microbes during assimilation and oxidation of organic material.

Nitrate EPA/74, 00620, p. 197

Reaction of nitrate ion with brucine in sulfuric acid to form a colored complex. The complex is measured colorimetrically and related to the nitrate concentration. See the method for interferences.

Sulfite EPA/74, 00740, p. 285 (W&WW/13, 158, p. 337)

The sample is titrated with standard potassium iodide-iodate solution. Oxidizable material interferes. See method for a discussion of interferences.

Thiocyanate J. M. Kruse and M. G. Mellon, Anal. Chem., 25, 446 (1953)

The sample is treated with copper sulfate and pyridine and the dipyridine - Copper (II) - thiocyanate complex which is formed is extracted into chloroform and measured colorimetrically.

Oil and Grease EPA/74, 00550, 00556 or 00560, pp. 226-235

Extraction with Freon and measurement of the Freon extractable material gravimetrically or by IR spectroscopy. Refer to methods.

TABLE V

RECOMMENDATION FOR SAMPLING AND PRESERVATION OF SAMPLES ACCORDING TO MEASUREMENT(1)

(Primary Reference: EPA/74)

Measurement	Volume Required (ml)	Container(2)	Preservative	Maximum Holding Time(6)
Acids, volatile	50	← unknown →		
Arsenic	100	P, G	HNO_3 to pH <2	6 Mos
BOD	1 000	P, G	Cool, 4°C	6 Hrs (3)
Carbon dioxide	100	G only		
COD	50	P, G	H_2SO_4 to pH <2	7 Days
Chloride	50	P, G	None Req.	7 Days
Cyanides	500	P, G	Cool, 4°C NaOH to pH 12	24 Hrs
Dissolved Oxygen				
Probe	300	G only	Det. on site	No Holding
Winkler	300	G only	Fix on site	No Holding
Fluoride	300	P, G	Cool, 4°C	7 Days
Metals				
Dissolved	200	P, G	Filter on site HNO_3 to pH <2	6 Mos
Suspended			Filter on site	6 Mos
Total	100		HNO_3 to pH <2	6 Mos
Mercury				
Dissolved	100	P, G	Filter HNO_3 to pH <2	38 Days (Glass) 13 Days (Hard Plastic)
Total	100	P, G	HNO_3 to pH <2	38 Days (Glass) 13 Days (Hard Plastic)
Nitrogen				
Ammonia	400	P, G	Cool, 4°C	24 Hrs (4)
Nitrate	100	P, G	Cool, 4°C	24 Hrs (4)
Oil and Grease	1000	G only	Cool, 4°C H_2SO_4 to pH <2	24 Hrs
Organic Carbon	25	P, G	Cool, 4°C H_2SO_4 to pH <2	24 Hrs
pH	25	P, G	Cool, 4°C Det. on site	24 Hrs
Phenolics	500	G only	Cool, 4°C H_3PO_4 to pH <4 1.0 g $CuSO_4$/l	24 Hrs

TABLE V (Cont'd.)

Measurement	Volume Required (ml)	Container(2)	Preservative	Holding Time(6)
Phosphorus				
Orthophosphate, Dissolved	50	P, G	Filter on site	24 Hrs (4)
Hydrolyzable	50	P, G	Cool, 4°C	24 Hrs (4)
Total	50	P, G	H_2SO_4 to pH <2 Cool, 4°C	24 Hrs (4)
Residue				
Filterable	100	P, G	Cool, 4°C	7 Days
Nonfilterable	100	P, G	Cool, 4°C	7 Days
Specific Conductance	100	P, G	Cool, 4°C	24 Hrs (5)
Sulfide	50	P, G	2 ml zinc acetate	24 Hrs
Sulfite	50	P, G	Cool, 4°C	24 Hrs
Thiocyanate	100	← unknown →		

(1) More specific instructions for preservation and sampling are found with each procedure.

(2) Plastic or Glass.

(3) If samples cannot be returned to the laboratory in less than 6 hours and holding time exceeds this limit, the final reported data should indicate the actual holding time.

(4) Mercuric chloride may be used as an alternate preservative at a concentration of 40 mg/l, especially if a longer holding time is required. However, the use of mercuric chloride is discouraged whenever possible.

(5) If the sample is stabilized by cooling, it should be warmed to 25°C for reading, or temperature correction made and results reported at 25°C.

(6) It has been shown that samples properly preserved may be held for extended periods beyond the recommended holding time.

Where possible, analyses should be performed as soon after sample collection as possible because as stated in EPA/74:

> "Complete and unequivocal preservation of samples, either domestic sewage, industrial wastes, or natural water, is a practical impossibility. Regardless of the nature of the sample, complete stability for every constituent can never be achieved. At best, preservation techniques can only retard the chemical and biological changes that inevitably continue after the sample is removed from the parent source. The changes that take place in a sample are either chemical or biological. In the former case, certain changes occur in the chemical structure of the constituents that are a function of physical conditions. Metal cations may precipitate as hydroxides or form complexes with other constituents; cations or anions may change valence states under certain reducing or oxidizing conditions; other constituents may dissolve or volatilize with the passage of time. Metal cations may also adsorb onto surfaces (glass, plastic, quartz, etc.), such as, iron and lead. Biological changes taking place in a sample may change the valence of an element or a radical to a different valence. Soluble constituents may be converted to organically bound materials in cell structures, or cell analysis may result in release of cellular material into solution. The well known nitrogen and phosphorus cycles are examples of biological influence on sample composition."

9. COAL AND COAL RELATED SOLID ANALYSIS

9.1 Introduction

Much attention has recently been focused on the analysis of coal, coal ash, fly ash, and airborne particulate matter for elemental composition. Atomic absorption spectrscopy, X-ray fluorescence, spark-source mass spectrometry, optical emission spectroscopy, and neutron activation have been applied for the analysis of these materials for trace elements (5-12). There is some disagreement in the literature as to which technique is best suited for the determination of a particular element.

A recent comprehensive study involving the analysis of 101 coals for trace elements, which was conducted by the Illinois Geological Survey, has appeared (15). Because of the extensive study of sample preparation techniques and methods of analysis given in this report, the methods described in it have been selected as the suggested procedures for the analysis of the coal and coal solids for trace elements where applicable. The measurement techniques which are used in the methods are given in Table VI. Some of the methods given in references 5-12 could be substituted for these as they have been also demonstrated to be valid. Perhaps the most important factor, besides the inherent detection limit in the selection of a method, is that experience with a method specifically for analysis of coal and coal related solids for a particular element is required before accurate, reliable results can be obtained.

In addition to the analysis of the solids for potential pollutants, it is desirable to analyze coal and related samples for ultimate and proximate compositions and to determine the ash fusion temperature. The results of these analyses may lend insight into the influence of various types of coals on pollutants in various plant streams. The suggested procedures for determining the values are given in Table VII.

9.2 Sampling

A gross coal sample should be collected as indicated in ASTM D-2234. ASTM D-2013 and D-271 describe the preparation of coal samples for analysis, and one of these methods should be used.

It is suggested that the collection of samples of coal ash and dump pit solids be performed as indicated in "Suggested Method for Sampling Iron Ores," ASTM 1974, Part 12, p. 792.

9.3 Preservation

The literature does not contain recommendations for the preservation of coal or coal ash samples. Therefore, it is suggested that these samples are stored in clean glass bottles equipped with polyethylene lined caps until analyses are performed.

TABLE VI

MEASUREMENT TECHNIQUES USED IN THE RECOMMENDED METHODS FOR ANALYSIS OF COAL AND COAL RELATED SOLIDS FOR TRACE ELEMENTS

(Details are given in reference 5)
(except for Ba and Li)

Element	Technique(1)	Detection Limit µg/g
As	NAA	1.2 in ash
Ba(2)	Emission Spectroscopy	Unknown
Be	OE-DR	1 in ash
Ca	XRF	12 in whole coal
Cd	AA	2.5 in ash
Cr	OE-DR	1.5 in ash
F	ISE	10 in whole coal
Fe	XRF	36 in whole coal
Hg	NAA	0.01 in whole coal
Li(2)	AA	Unknown
Mn	NAA	2 in whole coal
Na	NAA	0.5 in whole coal
Ni	OE-DR, AA, OE-P, XRF	1 in ash
Pb	AA, OE-DR	5 in ash
Se	NAA	1.8 in ash
V	OE-DR, OE-P, XRF	5 in ash

(1) NAA signifies neutron activation analysis.
OE-DR signifies optical emission, direct reading.
XRF signifies X-ray fluorescence.
AA signifies atomic absorption.
OE-P signifies optical emission photographic.
ISE signifies ion-selective electrode.

(2) Experiments must be performed to validate these techniques.

TABLE VII

SUGGESTED METHODS FOR GROSS COAL ANALYSIS

Component	Method
Moisture	ASTM D-271
Ash	ASTM D-271
Volatile Matter	ASTM D-271
Fixed C	ASTM D-271
S	ASTM D-271
P	ASTM D-271
C	ASTM D-271
H	ASTM D-271
N	ASTM D-271
Calorific Value	ASTM D-271 or D-3286
Fusibility of Coal Ash	ASTM D-1857

10. ANALYSIS OF COAL LIQUIDS

10.1 Introduction

As was stated earlier, much attention has been focused recently on the analysis of oils for trace quantities of metals (1-3). As the result of studies performed in conjunction with the Trace Metals Project involving the Atlantic Richfield Company, Chevron Research Company, Exxon Research and Engineering Company, Mobil Research and Development Corporation, and Phillips Petroleum Company and a study performed for the American Petroleum Institute (13) much insight has recently been gained on the analysis of oils for metals. These studies indicate that neutron activation analysis is applicable for the determination Sb, As, Co, Ma, Hg, Mo, Ni, Se, and V if they are present in oils in amounts greater than 5-50 ng/g, depending on the element, and that emission spectroscopy is applicable for the determination of Sb, Cd, Be, Cr, Co, Mn, Mo, Ni, and V if they are present in amounts greater than 20-50 ng/g. In addition to these techniques which give multielement analysis of samples, the members of the Trace Metals Project developed specific methods for the analysis of oils for Sb, Cd, As, Be, Cr, Co, Mn, Se, Mo, Ni, Se, and V to 10 ng/g. The methods developed during the course of the project have appeared in Analytical Chemistry and were the topic of an American Chemical Society Symposium held in conjunction with the National ACS Meeting in Philadelphia in April, 1975. The determination of trace quantities of metals in oils, other than those listed, has not been exhaustively studied, but other metals probably could be determined by modification of the techniques studied by the Trace Metals Project.

The selected methods for the analysis of oils for the elements listed in Table VIII are those developed by the Trace Metals Project for the individual elements, where available; and where unavailable, suggested methods for investigation to determine their applicability to oils are given. In some instances the multielement techniques may be preferable.

In addition to the analysis of coal liquids for metals, the analysis of these materials for polynuclear aromatic hydrocarbons, PAA's, is important because of the carcinogenic activity of some of these compounds.

The PNA analysis of [illegible] carried out by a gas chromatographic-ultraviolet spectrophotometric [illegible]. If the level is high with few interfering substances the ISW method [illegible] for "Tentative Method of Analysis for Polynuclear Aromatics in Coke Oven Effluents" is employed. A 1-10 microliter sample of the liquid would be injected into the GC and the appropriate peaks trapped and measured by UV.

If other high boiling organics are present, it is necessary to isolate an aromatic concentrate before the GC/UV step. The technique employed is presented in the ISM method 11104-04 73T. 0.5 grams of the liquid would be taken in a 100 ml beaker and spiked with radioactive B(a)A and B(a)P as directed in paragraph 7.1 of the procedure. The spiked sample would then be chromatographed on alumina as directed in paragraph 7.6.1. The procedure would then be followed as written.

10.2 Sampling

The collection of coal liquids samples over a period of time, and the preparation of composite samples for analysis is recommended.

10.3 Preservation

The storage of composite samples in Teflon bottles is recommended.

TABLE VIII

SUGGESTED METHODS FOR DETERMINATION OF METALS IN COAL LIQUIDS

Metal	Technique[1]	Reference[4]
As	Wet Digest/AsH_3 generation/AA	TMP
Ba	Wet Ash/ES	(2)
Be	Direct/HVAA	TMP
Ca	Wet Ash/AA	(2)
Cd	Wet Ash/HVAA or AA	TMP
Cr	Direct/HVAA	TMP
Fe	Wet Ash/AA	(2)
Hg	Wet Digest/CVAA	(2)
Li	Wet Ash/AA	(2)
Mn	Direct/HVAA	14
Na	Wet Ash/AA	(2)
Ni	Wet Ash/HVAA	TMP
Pb	Wet Ash/HVAA[3]	(2)
Se	Wet Digest/H_2Se generation/AA	TMP
V	Wet Ash/HVAA	TMP

(1) AA signifies flame atomic absorption.
HVAA signifies heated vaporization atomic absorption
CVAA signifies cold vapor atomic absorption
ES signifies emission spectroscpic.

(2) Methods have not been thoroughly investigated; in these instances, suggested techniques are given by the TMP which must be validated.

(3) Contamination from ambient sources of Pb could be a problem.

(4) TMP signifies method developed by the Trace Metals Project. Method has appeared in Analytical Chemistry.

TABLE IX

POLYNUCLEAR AROMATIC HYDROCARBONS WHICH ARE DETERMINED IN COAL LIQUIDS USING THE ISM METHODS

Benzo(k)fluoranthene
Benzo(b)fluoranthene
Benzo(a)pyrene
Benzo(e)pyrene
Perylene
Benzo(ghi)perylene
Coronene
Chrysene
Fluoranthene
Pyrene
Benzo(ghi)fluoranthene
Benz (a) anthracene
Triphenylene
Benzo(f)fluoranthene

TABLE X

OTHER ANALYSES

Total Sulfur	ASTM D-129, D-2622, or D-2784

11. ANALYSIS OF ATMOSPHERIC AND GASEOUS SAMPLES

11.1 Introduction

A variety of materials may be emitted to the air from coal gasification or liquefaction plants. Provision must be made to collect and analyze all components of interest, from heavy particulates to the most volatile gases and vapors. A great variety of sampling devices is needed for a complete sampling. Methods for collecting, measuring, and characterizing particulate matter are presented in Table XI. The best techniques for gases and vapors are in Table XII. Table XIII lists a number of direct reading indicator tubes. These are portable and convenient to use but at present many are only rangefinding and approximate in nature.

11.2 Particulates

The particulates in ambient air of the plant will be determined by the EPA specified method, "Reference Method for the Determination of Suspended Particles in the Atmosphere, High Volume Method, (High Vol.)." In this method, air is drawn into a covered housing and through a filter by means of a high-flow-rate blower at a flow rate (1.13 to 1.70 m^3/min; 40 to 60 ft^3 min) that allows suspended particles having diameters of less than 100 μm (Stokes equivalent diameter) to pass to the filter surface. Particles within the size range of 100 to 0.1 μm diameter are ordinarily collected on glass fiber filters. The mass concentration of suspended particulates in the ambient air (mg/m^3) is computed by measuring the mass of collected particulates and the volume of air sampled.

The particulates in the stack of the plant will be collected and measured by the EPA Method No.5, "Determination of Particulate Emissions from Stationary Sources." Where desirable, Monitaire samplers will be used to monitor the actual exposure of individual workers.

Total Particulate - In all cases total particulate will be determined gravimetrically by conditioning the filter, before and after use, in a constant humidity room and by weighing. This value will include both the inorganic and organic portions of the sample.

Particulate Size - Particulates are to be sized according to ASTM 2009.

Benzene Solubles - The benzene soluble components will be determined by extracting the particulates in a Soxhlet extractor using benzene. After extraction, the benzene will be removed and the solubles determined gravimetrically.

Characterization of Benzene Solubles - One of the objectives is to measure the concentration of individual PNA hydrocarbons, such as benzanthracene (BaA), Benzo(a)pyrene (BaP), and 12 others. In addition, it is desirable to obtain some overall compositional information. The methods to be employed are briefly described below.

Polynuclear Aromatic Hydrocarbons - Up to 14 polynuclear aromatic hydrocarbons will be measured by either the Intersociety Methods No. 11104-03 73T or ISM 11104-04-0473T depending on the complexity of the material. In the latter after the Soxhlet extraction, a sample to be analyzed is spiked with known quantities of carbon-14 labeled BaA and BaP. The sample is then transferred to a 100-ml beaker and evaporated, on a steam bath under nitrogen, to dryness as described earlier for the measurement of benzene solubles. This residue is dissolved in cyclohexane and caustic treated to remove some acidic compounds. Then a PNA hydrocarbon concentrate is obtained by solvent elution off a column of partially deactivated alumina. The solvents are cyclohexane, cyclohexane-benzene, benzene, and benzene-methanol. The fraction containing the PNA's is reduced to a small volume by evaporation on a steam bath. An aliquot of this sample is injected into a gas chromatograph and fractions are collected for measurement by UV and, in the case of BaA and BaP peaks, also for carbon-14 activity. These activities, compared with known concentrations originally added, give factors by which to relate the concentrations of each PNA to its total weight in the sample.

Other information on the nature of the benzene solubles will be obtained by gas chromatography, mass spectrometry, and UV and IR spectrophotometry. Elemental analysis for carbon, hydrogen, nitrogen, etc. will be done if necessary.

11.3 Gases and Vapors

C_1-C_5 Hydrocarbons - ASTM D-2820-72, page 950

G.C. analysis of a grab sample on a packed column operated isothermally at 0°C.

Benzene, Other Volatile Organics - NIOSH No.: 127

Adsorption on charcoal, desorption with carbon disulfide, G.C.

Carbon Monoxide - NIOSH No.: 112

Infrared analysis of a grab sample using a 10-meter-path-length gas cell.

Volatile Sulfur Compounds - (Hydrogen Sulfide, Carbonyl Sulfide, Carbon Disulfide, Mercaptans, Thiophenes, Sulfur Dioxide).
J. E. Chaney, J. of Gas Chromatography 4, 42, (1966).

A grab sample is taken in a 250-ml glass sampling tube through a Perma Dry tube to remove water. The compounds are separated by G.C. on a Triton X-305 or other suitable column and detected by a flame photometer or microcoulometer sulfur detector. Details on the detector are given in ASTM D-3246.

Total Sulfur - ASTM D-3246

Burning of sample oxygen in special tube to SO_2 followed by detections with microcoulometer.

Sulfur Dioxide - NIOSH No.: 163

Sulfur dioxide is absorbed and oxidized in 0.3N hydrogen peroxide, then titrated with barium perchlorate using Thorin as indicator.

Sulfuric Acid Mist - EPA Method 8 R-490

Sulfur trioxide is separated from the sulfur dioxide in a special collection apparatus and determined by the barium-thorin titration method.

Nitrogen Dioxide - 0.5-50 ppm - NIOSH No.: 108

Nitrogen dioxide is absorbed in an impinger containing an azo zye forming a stable pink color read at 550 nm on a spectrophotometer.

Nitrogen Dioxide - 5-1000+ ppm - EPA No.: 487

Grab sample collected in flask with oxidant, nitrogen oxide measured colorimetrically using the phenoldisulfonic acid procedure.

Aldehydes - MBTH Procedure

Aliphatic aldehydes are absorbed in impingers containing 3-methyl-2-benzothiazolone hydrazone hydrochloride (MBTH). The azine is oxidized by a ferric chloride-sulfamic acid solution and measured at 628 nm. Procedure of Hauser, T. R. et. al., Anal. Chem. 36 679 (1964).

Ammonia - ASTM D-1426

Ammonia absorbed in acid in impinger, distilled from alkaline solution and determined volumetrically or colorimetrically.

Phenols - ASTM D-1783

Phenol absorbed in alkaline solutions in impinger, distilled, reacted with 4-aminoantipyrine, and determined colorimetrically.

Cyanide - NIOSH No.: 116

The samples are taken using an impinger containing 0.1N NaOH. The samples are then analyzed using a cyanide ion specific electrode.

Arsine - ACGIH Method No.: 40

Arsine is collected in an impinger containing silver diethyldithiocarbamate. After sampling, the concentration is determined colorimetrically at 560 nm.

Mercury - EPA Method No.: 101 or 102, pages 512 and 521

The first method is used on samples that are primarily air, while the second is employed for hydrogen and other reducing gas streams. The mercury is collected in impingers containing acidic iodine monochloride solution. It is reduced to elemental mercury, aerated from the solution, and determined in a gas cell at 253.7 nm.

Beryllium Referee Procedure - EPA No.: 104, page 532

Sample is collected on Millipore filters and impingers containing distilled water. It is digested with acid and analyzed by atomic absorption spectrophotometry.

Beryllium Screening Procedure - EPA No.: 102, page 530

Sample is collected on a Millipore filter and analyzed by any acceptable method such as atomic absorption, spectrographic, fluorometric, etc.

Fluorides and Hydrogen Fluoride - NIOSH No.: 117

Samples are taken through impingers containing 0.1N NaOH, diluted with a buffer and analyzed using the fluoride specific ion electrode.

Nickel and Iron Carbonyls - Denshaw, et al., J. Appl. Chem., 13, 576, (1963).

Method could probably be extended to cobalt carbonyl.

Hydrogen Selenide - Collection in impingers containing Na_2CO_3 and measurement according to W. H. Alloway and E. E. Cary, Anal. Chem., 38, 1359 (1964).

Total selenium would be determined.

11.4 Direct Reading Colorimetric Indicator Tubes

Direct reading color indicator tubes have been used for the measurement of hydrogen sulfide and carbon monoxide for a number of years, and now there are more than a hundred different types in use. They are rapid, inexpensive, and are especially convenient for evaluation of toxic materials in industrial surroundings. At present, however, results may

be regarded as only approximate. The best accuracy that can be expected from indicator tubes of the better types is plus and minus 20 percent. Table XIII presents some of the tubes that may be applicable in coal conversion plants.

TABLE XI

SAMPLING AND ANALYTICAL METHODS FOR
PARTICULATES IN ATMOSPHERIC AND OTHER GASEOUS SAMPLES

Component	Method of Analysis
Particulates in Air (High Volume Sampler)	Code of Federal Regulations, Title 40, Appendix B. Environmental Protection Agency, U.S. Federal Register Office, "Reference Method for the Determination of Suspended Particles in the Atmosphere (High Volume Method)." ASTM D-2009-65.
Particulates in Stack Cases	ASTM D-2928; EPA Method No.: 5
Dust Fall	ASTM D-1739 - Collection and Analysis of Dustfall (Settleable Particles)
Benzene Soluble in Particulates	E. C. Tabor and D. H. Fair, J. Air Pollution Control Assoc., 11, 403 (1961).
Analysis of Benzene Soluble Portion of Particulate	
Polynuclear Aromatic Hydrocarbons 14 compounds including Benzanthracene and Benzo(a)pyrene	Intersociety Method 11104-03 73T "Tentative Method of Analysis for Polynuclear Aromatics in Coke Oven Effluents and ISM 11104-04 73T "Tentative Method of Analysis for Polynuclear Aromatic Hydrocarbons in Automobile Exhaust. Sensitivity is 1 $\mu g/m^3$ for each PNA.
Gas Chromatographic Analysis for Boiling Range	ASTM D-2887-72T "Boiling Range Distribution of Petroleum Fractions by Gas Chromatography."
Mass Spectrometric Method	N. E. Fitzgerald, V. A. Cirillo, and F. J. Galbraith, Anal. Chem. 34, 1276 (1962).
Infrared and Ultraviolet Spectra	
Carbon, Hydrogen, Nitrogen	R. D. Condon, Microchem. J. 10,408, 1966.
Sulfur	ASTM D-1552

TABLE XII

SAMPLING AND ANALYTICAL METHOD FOR ATMOSPHERIC AND OTHER GASEOUS SAMPLES

Component	Sample Collection	Method of Analysis	Sensitivity
Volatile Hydrocarbons (C_1-C_5)	Aluminized Bag	ASTM D-2820-72 "C_1 through C_5 Hydrocarbons in the atmosphere by Gas Chromatography"	0.01 ppm
Benzene, Toluene & Other Volatile Organics	Charcoal Adsorption	NIOSH Method No.: 127 "Organic Solvents in Air"	0.01 mg/sample
Carbon Monoxide	5-liter bomb or bag	NIOSH Method No.: 112	5 ppm
Volatile Sulfur Compounds: H_2S, SO_2, COS, RSH CS_2 thiophene	250 ml glass sample tubes	D. F. Adams and R. K. Koppe, Tappi, 42, 601 (1959); S. S. Brody and J. E. Chaney, J. of Gas Chromatography, 4, 42, (1966); F. V. Wilby, Am. Gas Assoc. Oper. Sect. Proc., Year 1965, pgs. 65-136.	1 ppm
SO_2 Only	Impinger	EPA Method No.: 6, NIOSH No.: 163	.25 ppm
Sulfuric Acid Mist and SO_2 emissions	Special EPA Train	EPA Method No.: 8	
Total Sulfur	250-ml glass tube	ASTM D-3246-73 "Sulfur in Petroleum Gas by Oxidative Microcoulometry"	
Nitrogen Dioxide			
High Levels	Special Flask	EPA Method No.: 8	3 ppm
Low Levels	Impinger	NIOSH Method No.: 108, ASTM D-1607-69, "Standard Method of Test for Nitrogen Dioxide Content of Atmosphere (Griess-Saltzman Reaction)."	.01 μg/liter
Aldehydes	Impinger	EPA MRTH Procedure, Hauser, T.R. Cummins R. L., Anal. Chem. (36) 679 1964	0.1 ppm
Ammonia	Impinger	ASTM D-1426, after collecting in acid in impinger	1 ppm
Phenols	Impinger	ASTM D-1783 after collecting in NaOH in impinger	1 ppm

TABLE XII (Continued)

Component	Sample Collection	Method of Analysis	Sensitivity
Cyanide	Impinger	NIOSH Method No.: 116	0.13 mg/m^3
Arsine	Silver Diethyldithiocarbamate in Impinger	Manual of A.C.G.I.H. "Determination of Arsenic in Air," NIOSH Method No.: 140	1 µg/sample
Mercury	Impingers with Iodine monochloride	EPA Method No.: 10	
Beryllium	Filter (screening) Impinger (reference)	EPA Method No.: 103 EPA Method No.: 104	.01 µg/m^3
Hydrogen Fluoride	NaOH in Impinger	NIOSH Method No.: 117 Fluorides and Hydrogen Fluoride in Air	.01 mg/m^3
Nickel and Iron Carbonyls	Impinger with Iodine monochloride	A.B. Densham, et al. J. Appl. Chem. 13, 576 (1963)	.01 ppm
Hydrogen Selenide	--	--	--

TABLE XIII

Some NCA Direct Reading Colorimetric Indicators

Substance	Measurable Range	Interference	Catalog Number
Arsine	0.005 - 1.0 ppm	Stibine, phosphine	[illegible]
Carbon Disulfide	5 - 500 ppm	--	[illegible]
Carbon Monoxide	10 - 1000 ppm	Hydrogen	[illegible]
Formaldehyde	1 - 100 ppm	Turpentine, other aldehydes	[illegible]
Hydrogen Chloride	2 - 500 ppm	HNO_3	[illegible]
Hydrogen Cyanide	1 - 65 ppm	Ammonia, H_2S	[illegible]
Hydrogen Fluoride	[illegible]	--	[illegible]
Hydrogen Sulfide	1 - 200 ppm	SO_2	[illegible]
Nitrogen Dioxide	[illegible] - 50 ppm	H_2S, Halides	[illegible]
Sulfur Dioxide	1 - 400 ppm	Acetic Acid	[illegible]

12. SAMPLE FORMAT FOR STREAM SAMPLING AND ANALYSIS

Sample formats to be completed for sampling and analyses are shown in Figures I and II.

FIGURE 1
SAMPLE SHEET FOR GROSS SAMPLE

Gross Sample No.

Date Taken: _____

Sample Size: _____ Time Taken: _____

Container: _____

Stream No.: _____ Location of Sample in Stream: _____

Flow Rate of Stream: _____

Pressure of Stream: _____

Temperature of Stream: _____

Sampling Procedure: _____

_____

_____

Disposition of Gross Sample: _____

_____

Interfering Substances: _____

Comments: _____

_____

_____

_____

Name of Person Taking Sample

FIGURE 11
SAMPLE SHEET FOR DETAILED SAMPLE

TO BE FILLED IN BY SAMPLER

Detailed Sample No. _____

(Use Gross Sample Number Followed by
a Dash and Number for Specific Sample)

Sample Size: _____ Date Taken: _____

Container: _____ Time Taken: _____

Preservative: _____ Analyze For: _____

To Be Filled In By Analyst

Date Analyzed: _____ Time Analyzed: _____

Analysis Method: _____

Method of Preparation: _____

Component Concentration: _____

Comments: _____

_____

_____

Analyst: _____

Date: _____

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